The Effects of Surface Anisotropy on Reaction Dynamics

by

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Abstract

Reaction dynamics of meta-diiodobenzene (mDIB) and trifluoromethyl (CF$_3$) was studied on the anisotropic Cu(110) surface at 4.6 K using Scanning Tunneling Microscopy (STM). Both systems were modeled by Density Functional Theory (DFT). The surface anisotropy, given by rows of Cu-atoms along the [11̅0] direction, was found to give three previously unreported outcomes: product rotation, bond-selectivity, and ‘surface-molecular-beams’.

In the electron-induced reaction of mDIB, iodophenyl product rotation was observed following single C-I bond dissociation in the major pathway. The rotation was shown to be caused by the attraction between the I-atom of the iodophenyl and the raised Cu-rows. In a minor pathway both C-I bonds were broken concurrently to give I-atoms from an un-rotated mDIB attributable to short iodophenyl lifetime. Since the extent of the iodophenyl rotation correlated with its rotational lifetime, the observed rotation could be used with the aid of theory to ‘clock’ the reaction dynamics.

Bond-selectivity was observed in the C-I electron-induced dissociation of physisorbed mDIB. The C-I bond directed along the Cu-row was found to dissociate with a hundred-fold greater probability than the C-I directed across the Cu-row. This large bond-selectivity was due to the
added electron impulsively propelling the system towards a lower energy barrier when the C-I bond was directed along the Cu-row, in which case C-Cu attraction stabilized the transition state.

Novel ‘surface-molecular-beams’ of a difluorocarbene (CF₂) ‘projectile’ were generated from the electron-induced dissociation of CF₃. In the beams the CF₂ projectile traveled unidirectionally along a Cu-row as far as ~50 Å, by translation-rotation coupling analyzed as ‘ratcheting’. In further work the CF₂ ‘projectile’ was aimed at a stationary CF₂ ‘target’ with selected impact parameter, and collision energy. At zero impact parameter and high collision energy the C₂F₄ product was formed recoiling ‘forward’, due to retention of translational energy along the direction of the incoming projectile. At low collision energy the C₂F₄ product recoiled ‘backward’, due to association reaction catalyzed by a raised surface Cu-atom.
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**Chapter 4: Surface Anisotropy gives Bond Selectivity**

**Figure 1.** STM images (EXPT) and simulations (TH) of initial and final states in the bond-selective reaction of mDIB. Panel (a) shows a physisorbed mDIB in DIAGONAL configuration. The molecule has two different C-I bond directions (blue lines): C-I(AL) points along the Cu-row, while C-I(AC) points across the Cu-row. The white cross indicates the center of the mDIB STM feature. Panel (b) shows the outcome for the reaction of C-I(AL). Panel (c) shows the outcome for the reaction of C-I(AC). Each alignment has a differently rotated IPh product. Both reactions give an I-atom, and a chemisorbed IPh, both chemisorbed. In the pictured final states (PIC) for each case, the broken C-I bond is marked by blue dashed line, and the IPh binds to the Cu-atom marked by green dashed circle. The STM images (2.5 × 1.7 nm\(^2\)) were obtained at sample bias of +0.1 V and current of 0.1 nA.

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Figure 1. Large-scale STM image (30.0 × 30.0 nm²) of Cu(110) surface at 4.6 K after dosing with CF₃I. The surface temperature rose up to ~14 K during the dose. The CF₃I molecules were observed to dissociate upon adsorption, giving pairs of I-atom (bright circular feature) and CF₃ (dim oval feature surrounded by a depression), both chemisorbed. A pair is indicated by two dashed circles in the Figure. The STM image was obtained at sample bias of −0.1 V and current of 0.5 nA.

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Figure 16. Two pathways of CF$_2$ + CF$_2$ association reaction based on the observed C$_2$F$_4$ recoil direction. Panel (a) illustrates the coordinate system. The direction of motion of the CF$_2$ projectile before it collides with the CF$_2$ target (blue line in Panel (a), denoted as $d_{\text{rec}}$(CF$_2$:proj)) was found to correlate with the recoil direction of the C$_2$F$_4$ product. The recoil of C$_2$F$_4$ ($d_{\text{rec}}$(C$_2$F$_4$)) measured from the prior position of CF$_2$ target (horizontal dashed line in Panel (a)), can be either ‘forward’ or ‘backward’. Panel (b) shows the C$_2$F$_4$ recoil ($d_{\text{rec}}$(C$_2$F$_4$, red axis) plotted against the recoil distance of the CF$_2$ projectile ($d_{\text{rec}}$(CF$_2$:proj), blue axis); low $d_{\text{rec}}$ corresponds to high E$_{\text{col}}$, high $d_{\text{rec}}$ to low E$_{\text{col}}$. .................................................................65

Figure 17. Computed dynamics for the ‘forward’ pathway in the CF$_2$ + CF$_2$ association reaction. The initial state (t = 0 fs) in this trajectory is constructed by introducing a zero-velocity CF$_2$ target into the I2S trajectory of a recoiling CF$_2$ projectile from Figure 6 at 163 fs. The CF$_2$ projectile reacts with CF$_2$ target on its first collision, giving a C$_2$F$_4$ recoiling ‘forward’. The grey vertical dashed line indicates the initial position of the center-of-mass of the CF$_2$ target. .................................................................67

Figure 18. Computed trajectory for ‘forward’ reaction superimposed on a restricted ground PES. The 2D-PES is constructed as a function of CF$_2$ projectile and CF$_2$ target tilt angles at constant center-of-mass separation. The computed trajectory, given as red line, involves the motion of 78 atoms in the system. The insets give the nuclear positions in the angle-angle space for the computed trajectory at different times, showing both CF$_2$ at their closest approach distance at 240 fs in Panel 1, the transition state at 265 fs in Panel 2, and the C$_2$F$_4$ product at 290 fs in Panel 3. The dotted black
lines in all Panels indicate C-Cu bond direction to an underlying Cu-atom. The dotted red line in Panel 2 indicates attraction at the inception of C-C bond formation, as evidenced by the negative slope of the potential towards the C$_2$F$_4$ product potential well at the transition state.

**Figure 19.** Computed dynamics for a ‘backward’ product scattering pathway in the CF$_2$ + CF$_2$ association reaction. The initial state (t = 0 fs) in this trajectory was constructed by introducing a zero-velocity CF$_2$ target into the I$_2$S trajectory of a recoiling CF$_2$ projectile from Figure 6 at 179 fs. The CF$_2$ projectile fails to react with the CF$_2$ target at the first collision. The second CF$_2$ + CF$_2$ collision, catalyzed by a raised Cu-atom, forms a ‘backward’ recoiling C$_2$F$_4$. The grey vertical dashed line indicates the initial position of the center-of-mass of the CF$_2$ target. The dashed circle behind the raised Cu-atom indicates the equilibrium position of the Cu-atom.

**Appendix A: Additional Surface-Aligned Reactions**

**Figure S1.** STM images (EXPT) of CF$_2$ + I-atom SAR with $b = 1.8$ Å. Panel (a) shows a CF$_3$ precursor chemisorbed at ~4.7 Å away from an I-atom. The CF$_3$ adsorbed on a Cu-row (white dashed line), while the I-atom adsorbed between two Cu-rows at a four-fold hollow site. The white cross defines the position where the tip was placed to induce the CF$_3$ reaction, while the black cross defines the initial position of the I-atom target. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the outcome where I-atom was displaced by ~2.4 Å along the Cu-row direction. The STM images (2.2 × 2.7 nm$^2$) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.

**Figure S2.** Data tally of successful and failed I-atom displacement due to CF$_2$ + I collision with $b = 1.8$ Å as a function of CF$_2$ projectile recoil distance prior to its collision with the I-atom target. Successful I-atom displacement was only observed when the CF$_2$ projectile recoiled less than ~5 Å prior to its collision, indicating that successful I-atom displacement requires an energetic CF$_2$ projectile. Note that 3.8 Å is the nearest possible CF$_3$ – I separation along [110] direction. Only cases where CF$_2$ was found within 2 unit cell along [110] from the I-atom in the final state were shown.

**Figure S3.** STM images (EXPT) of F + I SAR with $b = 3.3$ Å. Panel (a) shows a CF$_3$ precursor chemisorbed at ~4.6 Å away from an I-atom. The CF$_3$ adsorbed on a Cu-row (white dashed line), while the I-atom adsorbed between two Cu-rows at a four-fold hollow site. The white cross defines the position where the tip was placed to induce the CF$_3$ reaction, while the black cross defines the initial position of the I-atom target. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the outcome where I-atom was displaced by ~2.6 Å along the Cu-row direction. The STM images (3.4 × 4.1 nm$^2$) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.

**Figure S4.** Polar plot showing the angle and distance of I-atom target and the products in F + I SAR. The white cross indicates the position of the CF$_3$ precursor, while the red squares indicate the position of the I-atom relative to the CF$_3$. The data has been folded such that the I-atom target appears between 90° and 180°. The reaction of CF$_3$ precursor
broke a single C-F bond, giving an F-atom (green squares), and a CF$_2$ that recoiled along [1\overline{1}0] (not shown). This reaction caused the I-atom to be displaced to a new position (blue squares). The computed C-F bond directions in the CF$_3$ precursor is given as dashed lines. The distance between the concentric circles is 3.61 Å.

**Figure S5.** STM images (EXPT) of F + CF$_2$ SAR with $b = 0$ Å. Panel (a) shows a CF$_3$ precursor chemisorbed ~4.2 Å away from the CF$_2$ target. Both the CF$_3$ precursor and the CF$_2$ target were adsorbed on the same Cu-row (white dashed line). The white cross defines the position where the tip was placed to induce the CF$_3$ reaction. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the SAR outcome where a CF$_3$ product was formed on the same Cu-row. The STM images (2.8 x 3.4 nm$^2$) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.

**Figure S6.** STM images (EXPT) of F + CF$_3$ SAR with $b = 0$ Å. Panel (a) shows a CF$_3$ precursor chemisorbed ~7.6 Å away from the CF$_3$ target. Both the CF$_3$ precursor and the CF$_3$ target were adsorbed on the same Cu-row (white dashed line). The white cross defines the position where the tip was placed to induce the reaction of the CF$_3$ precursor, the black cross defines the initial position of the CF$_3$ target. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the SAR outcome, which consists of an F-atom product and a CF$_3$ product. The CF$_3$ product was found between the prior positions of the CF$_3$ precursor and the CF$_3$ target on the same Cu-row. The STM images (4.3 x 5.1 nm$^2$) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.

**Appendix B: Bonding Descriptions for F, CF$_2$ and C$_2$F$_4$**

**Figure S1.** Computed adsorption structures for F, CF$_2$, chemisorbed tetrafluoroethylene, C$_2$F$_4$, and physisorbed C$_2$F$_4$ shown as molecular models viewed from the top (PIC (TOP)) and the side (PIC(SIDE)). The C$_2$F$_4$ is ‘BENT’ is the chemisorbed state. Also shown from the side is the charge density difference ($\Delta \rho$) namely the change in electron distribution upon molecular adsorption ($\Delta \rho = \rho_{\text{adsorbate+surface}} - \rho_{\text{adsorbate}} - \rho_{\text{surface}}$). The color scale corresponds to charge gain of +0.02 e$^{-}$ Å$^{-3}$ (given as red), and charge loss of −0.02 e$^{-}$ Å$^{-3}$ (given as blue).

**Figure S2.** Gas-phase frontier molecular orbital of CF$_2$ and ‘BENT’ C$_2$F$_4$ showing the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) (isocontour: 0.007 e$^{-}$ Å$^{-3}$). The calculations were performed using Gaussian16.
<table>
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<td>AC</td>
<td>Across</td>
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<td>Local Density-of-States</td>
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<td>PAW</td>
<td>Projector Augmented Wave</td>
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<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<td>Abbreviation</td>
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<tr>
<td>pDOS</td>
<td>Projected Density-of-States</td>
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<tr>
<td>pes</td>
<td>Potential-energy Surface</td>
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<tr>
<td>Ph'</td>
<td>Meta-phenylene</td>
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<tr>
<td>SAR</td>
<td>Surface-Aligned Reaction</td>
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<td>Scanning Tunneling Microscope</td>
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<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum</td>
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<td>VASP</td>
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Chapter 1
Introduction

One of the holy grails in chemistry is the understanding and control of surface chemistry.\textsuperscript{1,2} The catalytic properties of metal surfaces have been known to depend on their structures\textsuperscript{3} as recently exemplified by facet-dependent catalytic activity in a metal nanoparticle\textsuperscript{4-7}. As a result, facet engineering of metal nanoparticles have emerged as a cost-effective solution to maximize the catalytic performance.\textsuperscript{8} Despite the progress in facet engineering, surface chemistry lacks insight on the fundamental question: ‘How does the facet characteristics influence a chemical reaction?’

The first step to address this question is to study the motion of adsorbed molecules during the course of their reactions in real-time and real-space.\textsuperscript{9-11} Real-time molecular dynamics which operate at sub-picosecond timescale can be obtained by pump-probe spectroscopy.\textsuperscript{12-14} However due to the lack of spatial resolution, these techniques could only probe the average dynamics of an ensemble. Alternatively, scanning probe microscopy does not provide real-time dynamical information, but allows real-space molecular dynamics to be inferred from the comparison between the molecule before and after the reaction.\textsuperscript{15-51} Localized excitation by a tip of a Scanning Tunneling Microscope (STM) has been used to energize an adsorbed molecule via electronic excitation\textsuperscript{18-32,39-43} or vibrational excitation\textsuperscript{31-38}, thereby enabling the study of reaction dynamics one-molecule-at-a-time.

In electronic excitation, reaction occurs via a transient molecular anion on the surface.\textsuperscript{31} The lifetime of such anion is short, in the order of few femtoseconds\textsuperscript{52,53}, and thus the motion involved in a chemical reaction, in the order of few picoseconds, occurs largely on the neutral, ground potential-energy surface, which can be heavily influenced by the surface structure. These dynamics have then been successfully rationalized in terms of \textit{ab-initio} models, employing quantum mechanical forces and classical motions.\textsuperscript{27-30,39-41,54}

This thesis presents the effect of surface anisotropy on the reaction dynamics in electron-induced reaction. The reaction dynamics was studied by STM on the anisotropic Cu(110) at 4.6 K, and supported by DFT calculations. The details for both experimental and theoretical methods are presented in the second chapter. The third to fifth chapter present the results and discussion. In
the third chapter, the surface anisotropy is shown to give a product rotation, which allows us to ‘clock’ reaction dynamics without a time-resolved STM. In the fourth chapter, the surface anisotropy is shown to give a bond-selective reaction between two chemically identical bonds, paving the way for site-selective surface reactions. In the fifth chapter, the anisotropy is shown to give ‘surface-molecular-beams’. The beam was aimed towards a stationary target, enabling the study of bimolecular reaction dynamics one-reaction-at-a-time. Finally, the thesis conclusions are given in the sixth chapter.
Chapter 2
Experimental and Theoretical Methods

2.1 Experiment

2.1.1 Ultrahigh vacuum chambers

The experiments were all conducted in an ultrahigh vacuum (UHV) environment with a base pressure $< 3 \times 10^{-11}$ mbar. This environment was required to prepare adequately clean surfaces by minimizing the surface contamination from the gas-phase. The UHV environment was achieved by differential pumping, and baking the chamber at 140 °C to remove molecules adsorbed on the chamber interior, which mainly consists of water.

2.1.2 Scanning tunneling microscope

The experiments were performed using a Scanning Tunneling Microscope (STM). The working principle of an STM is based on the quantum tunneling phenomenon. A simple 1-D tip-vacuum-sample tunneling junction of an STM is given in Figure 1 below, showing an electron tunneling through a potential barrier from the tip to a positively biased sample ($V_{\text{bias}} > 0$) which results in a tunneling current.

\[ I \propto V_{\text{bias}} \rho_s e^{-2kz} \]

**Figure 1.** One-dimensional schematic of the tunneling junction in an STM, showing an electron tunneling from the tip to a positively-biased surface ($V_{\text{bias}} > 0$) with a certain tip-sample separation ($z$).
where $I$ is the tunneling current, $V_{\text{bias}}$ is the bias applied to the surface, $\rho_s$ is the local density-of-states (LDOS) of the surface between $E_F + eV$ and $E_F$, $\kappa$ is the decay constant and $z$ is the tip-sample separation. The tunneling current is shown above to depend on the surface LDOS, an electronic factor, and the tip-sample separation, a topography factor. The exponential dependence of the current to the tip-sample separation results in orders of magnitude change in current when the separation is varied linearly, as evidenced in realistic systems\textsuperscript{56}. As a result, the majority of the tunneling current originates from the tunneling between the tip apex to the sample, which enables the STM tip to probe the sample at few Angstroms spatial resolution.

A more rigorous model of the tunneling current is given by Bardeen\textsuperscript{57}, where the rate of electron transfer from the tip-to-sample is determined by the Fermi golden rule\textsuperscript{58}. Bardeen showed that the probability for electron transfer increases as the wavefunction overlap between the tip and the sample increases. An important extension from Bardeen formalism is the Tersoff-Hamann approximation which greatly simplifies theoretical simulation of experimental STM images\textsuperscript{59,60}. By using an $s$-wave-tip model in the Bardeen formalism, Tersoff and Hamann shows that constant-current STM image is simply the LDOS contour of the sample between $E_F + eV$ and $E_F$, where $V$ is the potential of the sample relative to the tip.

The experiments presented in this thesis were all conducted in a commercial Omicron low-temperature STM (LT-STM) at 4.6 K. The LT-STM stage is cooled by a cooling block, as shown in Figure 2, which is located at the bottom of a liquid Helium (LHe) bath cryostat. The stage is thermally insulated from the environment by two inner radiation shields cooled by the LHe cryostat, which are surrounded by two outer shields cooled by a liquid Nitrogen (LN\textsubscript{2}) bath cryostat. The stage is suspended by springs, as shown in Figure 3, to vibrationally isolate it from the environment using the eddy-current damping system, shown in Figure 4.
Figure 2. A photograph showing the front view of the STM stage (Omicron LT-STM). Both the LHe and LN$_2$ shields have been removed to allow a clear view of the stage. The full assembly of the eddy-current damping stage is given in Figure 4.

Figure 3. The STM stage in the locked position (left photograph), and in the suspended position (right photograph).
All STM images shown in this thesis were obtained at 4.6 K in constant-current mode, where a constant current setpoint is maintained by a feedback loop, controlling the tip-surface separation throughout the scan. The bias reported in this thesis refers to the surface bias relative to the tip.

2.1.3 Sample and tip preparation

Figure 5. An Omicron Molybdenum-sample plate with a Cu(110) single-crystal. The spot-welded Ta-foil affixes the Cu-crystal in place. The Cu-crystal shown is 4 mm in diameter. The ‘eyelet’ of the plate provides a grabbing point by which the plate can transferred inside the UHV chamber.
The experiments were performed on a Cu(110) single-crystal (purchased from MaTeck), mounted on a Molybdenum-sample plate as shown in Figure 5 above. The Cu(110) surface was prepared by cycles of Ar-ion sputtering (beam energy: 0.6 keV, drain current ~ 7μA) and thermal annealing at 520 °C.

An STM image of a clean Cu(110) surface obtained at 4.6 K is given in Figure 6 below. The surface consists of two distinct directions: [11̅0], the direction of closed-packed rows of Cu-atoms; and [001], the direction across the Cu-rows. As shown in Figure 6, the surface possesses several high-symmetry sites, termed ‘atop’ for the site directly above a Cu-atom, ‘shortbridge’ for the mid-point between two Cu-atoms along [11̅0], ‘longbridge’ for the mid-point between two Cu-atoms along [001], and ‘four-fold hollow’ for the mid-point between four Cu-atoms.

![Figure 6. STM image of a clean Cu(110) surface at 4.6 K with atomic resolution obtained at bias +10 mV and current 50 nA. The white rectangle box indicates the unit cell of the surface (dimensions: 2.55 Å along [11̅0] and 3.61 Å along [001]).](image)

The STM tip was prepared by electrochemically etching a W-wire (diameter: 0.375 mm) by ~3 M NaOH solution using the setup shown in Figure 7 below. The etched tip was rinsed by water, isopropanol and acetone before introducing it into the UHV chamber.
2.1.4 Dosing molecules to the surface

In Chapter 3 and 4 of this thesis, meta-diiodobenzene (mDIB, Sigma-Aldrich, 98%) was used, while in Chapter 5, trifluoriodomethane (CF$_3$I, Synquest, 99%) was used. Meta-diiodobenzene was degassed by direct pumping using a turbomolecular pump before dosing, while trifluoriodomethane was used without further purification. The molecule was dosed onto the clean Cu(110) surface via a capillary tube pointed towards the cooled STM stage. During the dose, the temperature rose from 4.6 K to ~13 K.

2.1.5 Electron-induced reaction

The adsorbed molecule was imaged by STM prior to its reaction which was initiated by the electron from the STM tip, as exemplified in Figure 8 below.

The reaction was induced following the procedure below:

- The tip was positioned above the molecule (for example, see white cross in Figure 8 above), and afterward, the tip height was adjusted.
Feedback-loop was deactivated, and the bias was ramped up to $V_{\text{pulse}}$. The tunneling current was measured as a function of time up to 10 seconds in which a reactive event was identified by a discontinuity in the current-vs-time curve as exemplified in Figure 9 below.

![Image](image.png)

**Figure 9.** An example of current versus time plot. A single discontinuity indicates a reactive event occurring under the tip. The time (T) and average current (I) before the discontinuity were recorded for analysis.

By comparing the STM images before and after the electron-induced reaction, as exemplified in Figure 8, the recoil distance and direction of the products from the initial reagent could be obtained. The analysis of the STM images were performed using the WSxM software.\(^{61}\)

### 2.1.6 Determining the reaction rate

The number of electron required to induce a reaction can be obtained by measuring the reaction rate as a function of tunneling current. For a reaction with a single pathway, the average reaction rate can be obtained by previously established methods.\(^{31,62}\) In this thesis, the method has been extended to address a case where a reaction has two competing pathways: X and Y, as in the case for the reaction of mDIB on Cu(110).

For every electron that impinges upon an adsorbed molecule, three different outcomes are possible: no-reaction, reaction X and reaction Y. Such a process can be modeled by a trinomial distribution, where the probability of observing reaction X at the $N$-th attempt is:

$$P_X(N) = p_X(1 - p_X - p_Y)^{N-1}$$

where $p_X$ and $p_Y$ are the probabilities of observing reaction X and reaction Y per attempt. For $N \to \infty$, $p_X \ll 1$ and $p_Y \ll 1$, the expression above can be approximated by:

$$P_X(N) = p_X e^{-N(p_X + p_Y)}$$
The number of attempts \((N)\) can be thought of as the number of electrons that have impinged on the molecule before it reacts:

\[
N = \frac{I \times T}{e}
\]

where \(I\) is the tunneling current, \(e\) is the elementary charge, and \(T\) is the elapsed time before the discontinuity in the current versus time curve, which is exemplified in Figure 8 above. Hence, the probability of observing reaction X by the \(N\)-th attempt, can be replaced by:

\[
P_X(T) = p_X e^{-IT(p_X+p_Y)/e}
\]

And similarly for reaction Y:

\[
P_Y(T) = p_Y e^{-IT(p_X+p_Y)/e}
\]

Given that the decay constants in the expression for \(P_X(T)\) and \(P_Y(T)\) are identical, we have used the experimental \(P_X(T)\) curve to obtain both \(p_X\) and \(p_Y\). Figure 10 shows an example of a \(P_X(T)\) curve obtained by binning the elapsed times before a discontinuity in all current-versus-time curves that gave reaction X. The results presented in this thesis are not sensitive to the choice of bin numbers, but for consistency, the Doane’s formula\(^{63}\) was used as the binning procedure.

**Figure 10.** Histogram obtained from the experiment (black bars) showing the normalized probability to observe reaction X at various time \((P_X(T))\). The histogram is fitted with a single-parameter exponential function \((e^{-AT})\), plotted as the red line in the Figure. The total number of data points shown were 433.

The decay constant \((A)\) obtained from the single-parameter exponential fit \((e^{-AT})\) to the experimental \(P_X(T)\) versus \(T\) curve can be equated to our statistical model, giving:
\[ A = \frac{I}{e} (p_X + p_Y) \]

Given that in our experiment we pulsed the molecule until we observe either reaction X or Y, the proportion of reaction X at current \( I \) from the experiment is therefore:

\[
\frac{N_X}{N_X + N_Y} = \frac{p_X}{p_X + p_Y}
\]

where \( N_X \) is the number of outcome X in the experiment, and \( N_Y \) is the number of outcome Y. It follows that:

\[
p_X = \frac{eA}{I} \times \frac{N_X}{N_X + N_Y}
\]

\[
p_Y = \frac{eA}{I} \times \frac{N_Y}{N_X + N_Y}
\]

where \( p_X \) and \( p_Y \) are the yield (probability of reaction per electron) for X and Y.

Hence, to solve for \( R_X \) which is defined as the number of outcome X per unit of time:

\[
R_X = \frac{N \times p_X}{T} = \frac{IT \times p_X}{eT} = A \times \frac{N_X}{N_X + N_Y}
\]

Likewise for \( R_Y \):

\[
R_Y = A \times \frac{N_Y}{N_X + N_Y}
\]

By plotting \( R_X \) and \( R_Y \) against the tunneling current in a log-log scale, the number of electrons required in pathways X and Y can be determined.

In the simplified case where only a single reactive outcome X is observed, the expression reduces to:

\[
p_X = \frac{eA}{I}
\]
\[ R_X = \frac{N \times p_X}{T} = \frac{IT 	imes p_X}{eT} = A \]

where \( p_X \) is the yield (probability of reaction per electron) for outcome X, \( R_X \) is the reaction rate for outcome X, \( I \) is the tunneling current, and \( e \) is the elementary charge.

### 2.2 Theory

#### 2.2.1 Density functional theory

To account for the experimental findings, Density Functional Theory (DFT) calculations were performed. The calculations were conducted at SciNET supercomputer\(^{64} \) using plane-wave basis sets in Vienna Ab-initio Simulation Package (VASP)\(^{65,66} \). The calculations used generalized-gradient approximations (GGA), projector augmented wave (PAW) method\(^{67,68} \), and Perdew-Burke-Ernzerhof (PBE) functional\(^{69} \). Gamma-point sampling was used for structure relaxations, nudged elastic band (NEB) calculations with climbing-image method\(^{70} \) for minimum energy pathway calculations, projected density-of-states (pDOS) calculations and molecular dynamics (MD) trajectories. The pDOS was computed using Gaussian smearing (\( \sigma = 0.25 \text{ eV} \)). All molecular structures presented in this thesis were visualized using the VESTA software\(^{71} \).

The Cu(110) surface was modeled by a slab consisted of 5 layers of Cu-atoms with a vacuum gap of more than 15 Å. In all adsorption structures presented, all atoms were relaxed, except for the bottom two layers of the Cu-slab, until the residual force on each atom was < 0.01 eV/Å. In all calculations, dipole corrections were activated along the surface normal.

The STM appearance of an adsorbed molecule and its subsequent reaction products were interpreted by STM simulation, which was performed via the Tersoff-Hamann approximation\(^{59,60} \) using the calculated wavefunction of the relaxed structures from VASP and visualized using the Hive software\(^{72,73} \).

We have used two set of parameters in this thesis. The calculations in Chapter 3 and 4 were done using VASP 5.2.11, and a parameter set identical to earlier works in this lab to allow comparison\(^{27-30} \). The calculations in Chapter 5 were done using VASP 5.4.1, and a different parameter set.
In Chapter 3 and 4, a (6×6) Cu-slab, consisting of 180 Cu-atoms, was used. The dispersion forces were included by 2nd version of Grimme’s semiempirical correction (DFT-D2) (ref 74), and an energy cutoff of 450 eV was used. Due to the known overestimation of the physisorption energy by PBE and DFT-D2 (ref 75), the adsorption energy of the molecule were calculated using RPBE functional (ref 76), DFT-D2, a denser k-mesh (3×3×1) from the relaxed structure obtained by PBE and DFT-D2.

In Chapter 5, a (4×6) Cu-slab, consisting of 120 Cu-atoms, was used for all calculations, except for MD calculations, which used a (3×8) Cu-slab. The dispersion forces were included by DFT-D3 (ref 77), and an energy cutoff of 400 eV was used. The adsorption energy was computed from a structure relaxed using PBE functional, DFT-D3, and a denser k-mesh (3×3×1).

The pDOS of chemisorbed CF₃, studied in Chapter 5, was further assessed by projecting a molecular orbital (MO) of gaseous CF₃ into the pDOS, following the procedure described by Lorente.⁷⁸,⁷⁹ The MO chosen was C-F σ* anti-bonding molecular orbital, obtained from a gaseous CF₃ with its structure distorted to its chemisorbed geometry. The anti-bonding MO was projected to the pDOS of CF₃ chemisorbed on the surface, following the equation below:

\[ \rho'(E) = \sum_{\lambda} |\langle MO|\lambda\rangle|^2 \delta(\epsilon_{\lambda} - E) \]

Where \( \lambda \) is a label for an eigenstate with an energy \( \epsilon_{\lambda} \) in the CF₃ chemisorbed on the surface, and MO is the label for the C-F anti-bonding molecular orbital for the gaseous CF₃ distorted to its chemisorption geometry. This projection revealed the C-F anti-bonding character for each eigenstate of the CF₃ chemisorbed on the surface.

The NEB calculations with climbing image method⁷⁰ was used to determine the minimum energy pathway on the ground potential-energy surface. In one calculation, up to five intermediate images prepared by linear interpolation, were used between the relaxed initial state and final state. The calculations were conducted until the forces orthogonal from the band were < 0.02 eV/Å.
2.2.2 Impulsive two-state model

Figure 1. The Impulsive Two-State (I2S) model shown here schematically employed to simulate the electron-induced reactions studied in this thesis. The system is evolved for a short time (t*) on an anionic potential-energy surface (pes*), illustrated by the red line. The position and momentum for every atom at the end of t* is continued on the ground potential-energy surface (pes), given by the black line, until the system settles into a potential-well.

The electron-induced dissociations of molecules studied in this thesis were simulated by the Impulsive Two-State (I2S) model, which employs an empirical anionic potential-energy surface (pes*)\(^8\) and a neutral ground-state potential-energy surface (pes). To simulate the electron occupation of Carbon-Halogen anti-bonding orbital, common in the system studied in this thesis, an electron was added to the Halogen atom of the reagent (as described below) to introduce a repulsion between the Carbon and the Halogen atom. This repulsion obtained at the pes* introduces momentum which is transferred to the ground pes, enabling the system to overcome a reaction barrier on the ground pes as illustrated in Figure 11 above. This is similar to the Menzel-Gomer-Redhead (MGR) scenario of molecular desorption by low-energy electrons.\(^8\)

Using MD, as shown in Figure 11 above, trajectories were computed by first transferring the initial state to pes* where it was evolved for a time t*. The system was then brought to the ground pes by removing the added electron on the Halogen-atom. Continuing from the geometry and velocities obtained from pes* at the end of t*, the trajectory was computed on ground-pes until the system settles on a specific potential well. The final states were relaxed, and compared with the product distributions observed in the experiment.
The anionic pseudopotential was approximated by transferring x electrons (0 ≤ x ≤ 1) from the inner shell of the Halogen-atom to its valence shell. For the case of I-atom in Chapter 3 and 4, x electrons was transferred from the 4d orbital to the 5p orbital, to yield pseudo-ionic configuration: [Kr] 4d^{9-x} 5s^2 5p^{5+x}. For the case of F-atom in Chapter 5, to obtain the anionic pseudopotential for F-, one electron was transferred from the 1s orbital to the 2p orbital, to yield pseudo-ionic configuration: [He] 2s^2 2p^6.

To simulate the effect of added charge, an attractive Coulombic interaction due the induced image charge was added to calculations involving pes*. The ionic atom is assumed to be a point charge, –Q, located at some distance, d, above the Cu-surface, which induces an image charge, +Q, located at the exact distance, d, below the surface. The correction introduces an attractive force on the ionic atom towards its image charge along the surface normal axis (z-axis) as follows:

\[ \vec{F} = -\frac{Q^2}{4\pi\varepsilon_0 (2d)^2} \hat{z} \]

The total energy of the system was corrected by the image-charge interaction, as follows:

\[ E = -\frac{Q^2}{4\pi\varepsilon_0 (2d)} \]

The MD calculations were computed under microcanonical condition which conserved the number of the atoms (N), the volume (V), and the total energy of the system (E). The initial state was initialized by a set of random initial velocities on each atom from the Maxwell-Boltzmann distribution at 4.7 K. The MD calculations used a 0.5 fs time step which gave a negligible total energy-drift < 0.04 eV/ps.
Chapter 3
Surface Anisotropy gives Product Rotation

This chapter is adapted with permission from Anggara, K. et al. Clocking Surface-Reaction by In-plane Product Rotation. *J. Am. Chem. Soc.* 138, 7377–7385 (2016). Copyright 2018 American Chemical Society. K.A. was involved in the STM experiments and conducted the *ab-initio* calculations.

### 3.1 Introduction

Rotation is one of the fundamental modes of motion of a molecule. Gas phase reaction dynamics showed that molecular rotational period can be utilized as a means to clock a reaction. For example, in the photodissociation of iodobenzene, the degree of anisotropy in product scattering is indicative of how promptly the bond breaks following the photoexcitation. Rotation also contributes to molecular machines commonly encountered in biological systems. On surfaces, the rotation of molecules can be initiated by thermal energy, photon or electron. Here, we have the studied rotation of a molecule initiated by a chemical reaction at an anisotropic surface, and have proposed that the rotation be used to clock the reaction dynamics. The role of an anistropic surface is pivotal in this work since it was found to be the cause of the molecular rotation.

Electron-induced reaction of meta-diiodobenzene (mDIB) was studied on Cu(110) at 4.6 K by Scanning Tunneling Microscopy (STM). The reaction broke the C-I bond of the molecule, giving I-atoms that recoiled along the prior bond direction, as also found in the reaction of para-diiodobenzene and ortho-diiodobenzene on the same surface. Two distinct reaction pathways were observed in the present work: SUCCESSIVE and CONCERTED. In the SUCCESSIVE pathway, one electron broke one C-I bond, giving meta-iodophenyl (IPh) product that had rotated in-plane by three different amounts. This in-plane rotated of IPh was confirmed by breaking the C-I bond in the IPh product, giving I-atoms that ended up at three distinct angles. In the CONCERTED pathway, one electron broke two C-I bonds, giving I-atom products that originated from an IPh that had not rotated. Molecular dynamics calculations employing the Impulsive Two-State (I2S) model showed a positive correlation between the rotational...
lifetime of IPh and the extent of IPh rotation. The in-plane rotation was computed to originate from the attraction between the I-atom in IPh and the Cu-atoms arranged anistropically on the surface. Interestingly in the CONCERTED pathway, the IPh did not rotate, because its rotational lifetime was cut short by the rupture of its C-I bond. Given that the extent of IPh rotation serves as a clock of the reaction dynamics, measuring the direction of recoil of I-atom product from a rotating IPh at successive times could provide an experimental means to time-resolve reaction dynamics. The significance of this is that it would enable studies of time-resolved dynamics at subpicosecond intervals, using a conventional STM.

3.2 Results and discussion

3.2.1 Physisorbed initial state

Figure 1. Large-scale STM image (50.0 × 50.0 nm²) of Cu(110) surface at 4.6 K after dosed with mDIB. The mDIB molecules were observed to adsorb intact on the surface in two different alignments: ‘ROW’ (R) and ‘DIAGONAL’ (D). The image was obtained at sample bias of +0.2 V and current of 0.2 nA.
Figure 1 shows meta-diiodobenzene (mDIB) adsorbed intact on the Cu(110) surface after dosed at a 12.6 K surface. The molecule was imaged as a kidney bean shaped protrusion with an apparent height of 1.29 ± 0.04 Å. Two physisorption geometries can be distinguished based on the alignment of the molecule C₂-axis with respect to the underlying Cu-row: ‘ROW’ (major species, 56 ± 5%) has its C₂-axis parallel to the Cu-row, and ‘DIAGONAL’ (minor species, 44 ± 5%) has its C₂-axis turned ~57° away from the Cu-row. The electron-induced reaction of both species was studied at 4.6 K. This chapter focuses on the reaction dynamics of ‘ROW’ initial state. The reaction dynamics of ‘DIAGONAL’ will be discussed in the next chapter.

Figure 2a below shows the STM appearance of ‘ROW’ physisorbed state (EXPT) and its STM simulation (TH). DFT calculations show the molecule adsorbs with its aromatic ring parallel to the surface plane, and both its C-I bonds pointing 61° away from the Cu-row direction. This geometry is computed to be the most stable adsorption geometry of mDIB on Cu(110) (E_{ads} = 1.04 eV) in agreement with previous calculations by Panosetti and Hofer. 93

3.2.2 Electron-induced reaction

Reactions of ‘ROW’ on the surface can be induced by tunneling electrons at a surface bias above +1.1 V. Two reaction pathways were observed: SUCCESSIVE (97.3 ± 3.0%) and CONCERTED (2.7 ± 0.3%). In the SUCCESSIVE pathway, a single electron breaks one C-I bond of mDIB one-at-a-time. The first C-I bond-breaking gives an I-atom and a meta-iodophenyl (IPh), while the second C-I bond-breaking gives another I-atom and a meta-phenylene (Ph’). In the CONCERTED pathway, a single electron breaks both C-I bonds of mDIB, giving two I-atoms and a Ph’.
3.2.3 SUCCESSIVE pathway

Figure 2. STM images (EXPT) and simulations (TH) of initial and final states in the SUCCESSIVE pathway. Panel (a) shows a physisorbed mDIB in ROW configuration shown with its C$_2$-axis (black line). The white cross indicates the center of the mDIB STM feature. The STM simulation (TH) shows the direction of both C-I bonds of mDIB (blue lines). Panels (b) to (d) show the products of the first C-I bond-breaking: chemisorbed IPh and I-atom(#1) in three different alignments (A, B and C). Each alignment has a differently rotated IPh product. The three IPh products were computed to bind to the same Cu-atom (white dashed line) and have different C-I bond direction (black dashed line). Panel (b’) to (d’) show the products of the second C-I bond-breaking: chemisorbed Ph’ and I-atom(#2) in the three different alignments (A’, B’ and C’). Each alignment has a differently aligned Ph’ and I-atom(#2) that recoiled in a specific direction (white line). The STM images (2.0 × 2.0 nm$^2$) were obtained at sample bias of +0.1 V and current of 0.2 nA.

The first C-I bond-breaking of mDIB in the SUCCESSIVE pathway gives I-atom(#1) and an IPh as reaction products. Figure 2b to 2d show the STM images (EXPT) and simulations (TH) of the three different alignments of the reaction products: A (26.5 ± 1.6%), B (28.5 ± 1.7%), and C (38.5 ± 1.9%). In all these alignments, the IPh was imaged as an oval protrusion with an apparent height of 1.07 ± 0.04 Å. DFT calculations confirmed the existence of three potential wells that
correspond to alignments A, B and C. The adsorption energy of a single IPh was computed to be 2.17 eV in alignment A, 2.47 eV in B and 2.39 eV in C. In the TH panel of Figures 2b to 2c, STM simulations show that the bright spot in the STM image of IPh approximates the position of the I-atom in the IPh. The calculations also show that the IPh in alignment A, B and C binds to the same Cu-atom located underneath the prior intact mDIB reagent (white dashed circle in Figure 1b to 1d). A small number of cases (6.5 ± 0.8%) gives the IPh bound 1 – 2 unit cell along the [1\bar{1}0] away from the binding site of IPh in A, B and C.

**Figure 3.** Distance and angle distributions of the products in the SUCCESSIVE C-I pathway. Panel (a) shows the distribution of I-atom(#1) (black squares) and IPh (red squares) from the first C-I bond-breaking. The data has been folded so that I-atom(#1) is located in the left of the polar plot. The blue line indicates the directions of the C-I bond in the mDIB initial state. Panel (b) shows the distribution of I-atom(#2) (blue squares) and Ph'-A (green squares) from the second C-I bond-breaking. The black dashed line indicates the computed C-I bond direction of IPh in alignment A. Panel (c) and (d) show the data for IPh initial state in alignment B and C. In all of the polar plots, the origin is the white cross (center of intact mDIB molecule), and the distance between concentric circles are 3.61 Å. Colored ticks on the polar plot give the average recoil angle of the products. All angles are measured clockwise from the [1\bar{1}0].

Product alignments A, B and C are distinguished based on the position of the I-atom in the IPh relative to the surface plane. As shown in Figure 3a, the IPh was located at: 86° for alignment A,
138° for B, and 185° for C with respect to [1\bar{1}0]. This shows that the IPh has rotated in-plane to three different angles. The pivot of this rotation was computed to be the Cu-atom to which the IPh was bonded (shown as dashed circle in Figures 1b to 1d, TH).

In alignments A, B and C, I-atom(#1) was observed to recoil 73 ± 14° away from the [1\bar{1}0] direction (shown as 287° in Figure 3a). This shows that the I-atom(#1) was scattered along the computed C-I bond direction of the intact mDIB at 61° from [1\bar{1}0] as observed in earlier work.\textsuperscript{19,20,24,27–30,39–41,48–50} This result implies that prior to the C-I bond-breaking event there was no in-plane rotation in the intact mDIB. As a result the observed IPh rotation can be concluded as an event that occurs after the C-I bond breaks, as confirmed by MD calculations below.

The IPh in-plane rotation was further confirmed by inducing the second C-I bond-breaking i.e. the C-I bond in IPh. The second bond-breaking gives I-atom(#2), and a meta-phenylene (Ph’) as shown in Figure 2b’ to 2d’. Figure 3b to 3d show that each IPh alignment gives I-atom(#2) at a unique location with respect to [1\bar{1}0]: 85° for alignment A, 136° for B, and 179° for C. The correspondence between I-atom(#2) angles and the IPh angles confirms that the I-atom in IPh has been displaced to three different angles as a consequence of IPh in-plane rotation in the first C-I bond-breaking event.
Figure 4. Three different chemisorbed Ph' from the second C-I bond-breaking in the SUCCESSIVE pathway. Panel (a) shows STM images (2.0 × 2.0 nm$^2$) obtained at sample bias of +0.1 V and current of 0.2 nA. The height profile of the Ph' is given along the [001] direction. Panel (b) shows the computed structure for the vertical Ph'-B and its spin density ($\rho = \rho_{\text{spin-up}} - \rho_{\text{spin-down}},$ isocontour = 0.0005 e Å$^{-3}$). Ph'-B in its electronic ground-state (total magnetic moment ~ 1 $\mu_B$) possesses a C-dangling bond pointing away from the surface. Only positive spin density is shown.

The IPh in alignment A, B and C was found to selectively produce different configuration of chemisorbed Ph'. Figure 4a shows the STM image of three Ph' observed in the experiment. In more than half of the cases examined (>65%), IPh in alignment A gives Ph'-A of 0.55 ± 0.04 Å in height; IPh in B gives Ph'-B of 0.97 ± 0.04 Å in height; and IPh in C gives Ph'-C of 0.32 ± 0.04 Å in height. Ph'-A and Ph'-C found here are similar in height to the Ph' with a nearly horizontal ring observed on Cu(111)$^{94,95}$, while Ph'-B is similar in height to structures containing a vertical ring on Cu(110)$^{23,25,40}$

DFT calculations as given in Figures 2b' to 2d' (TH panels) show that all three Ph' adsorbs differently to the surface: Ph'-A adsorbs between two Cu-rows, Ph'-B adsorbs between two adjacent Cu-atoms on a Cu-row, and Ph'-C adsorbs between two non-adjacent Cu-atoms on a Cu-
The rings of Ph’-A and Ph’-C were computed to be nearly horizontal, while that for Ph’-B was computed to be vertical. The spin-polarized calculation for Ph’-B, pictured in Figure 3b, shows that the molecule has a C-dangling bond that is pointing away from the surface.

3.2.4 CONCERTED pathway

![MINOR PATHWAY: CONCERTED C-I](image)

**Figure 5.** STM images (EXPT) and simulations (TH) of initial and final states in the CONCERTED pathway. Panel (a) and (b) show the initial and final states of the reaction, where both C-I bonds have broken, giving two I-atoms and a Ph’. The white cross indicates the center of the mDIB STM feature. The blue lines indicate the C-I bond directions in the intact mDIB reagent. The STM images (2.0 × 2.0 nm²) were obtained at sample bias of +0.1 V and current of 0.2 nA. Panel (c) shows the distance and angle distribution of the reaction products. The origin of the polar plot is the white cross (center of intact mDIB molecule), and the distance between concentric circles are 3.61 Å. Colored ticks on the polar plot give the average recoil angle of the products. All angles are measured clockwise from the [110].

A variant of C-I bond-breaking dynamics in the electron-induced of mDIB was observed as the minor pathway, termed CONCERTED. The reaction breaks both C-I bonds in mDIB, giving two I-atoms and a chemisorbed Ph’ as shown in Figure 5a and 5b. Figure 5c shows that both I-
atoms were observed to scatter symmetrically ±73° away from the Cu-row direction (shown as 74° and 288° in Figure 5). The I-atoms were found to recoil along its prior bond direction as these angles resemble the computed C-I bond direction in the mDIB reagent (±61° away from the Cu-row direction). The position and height of the formed Ph’ was found to be similar to Ph’-A observed in the SUCCESSIVE pathway (shown in Figure 2b’). Thus the product alignment in the CONCERTED pathway indicates that in-plane rotation is absent in the reaction dynamics.

3.2.5 Reaction mechanism

![Figure 6](image)

**Figure 6.** Evidence for electron-induced reaction. Reaction rate is plotted in a log-log plot against the tunneling current for the C-I bond-breaking reaction in the SUCCESSIVE pathway (black squares) and for the CONCERTED pathway (red circles). The reaction rates were measured at +1.4 V. Linear fit of the data points give a slope of \( n = 1.0 \pm 0.2 \) for the SUCCESSIVE pathway, and \( 1.2 \pm 0.1 \) for the CONCERTED pathway. The error bar is standard error of the exponential fitting of the data (see Methods for details).

The evidence that the reaction of mDIB is initiated by electron is given by the reaction rate plotted against the tunneling current shown in Figure 6. The average reaction rate at each tunneling current was determined by modifying the previous methods.\(^{31,62}\) In present work, the binomial distribution used in the previous methods was modified to a trinomial distribution (see Methods for details). This modification is necessitated by the two outcomes in the reaction of mDIB i.e. first C-I bond-breaking in the SUCCESSIVE pathway or both C-I bond-breaking in the CONCERTED pathway. The reaction rates measured at +1.4 V for both pathways of mDIB reaction were found to vary linearly with respect to the tunneling current, indicating that one electron is required to induce the reaction. The linear dependence between reaction rate and tunneling current also excludes electric field as the cause of the observed reaction.\(^{23}\)
Figure 7. Projected density-of-states (pDOS) of the physisorbed mDIB in ROW configuration. The lowest unoccupied molecular orbital (LUMO) is located 0.9 eV above the Fermi level. The solid, dashed and dotted lines give the pDOS of the mDIB molecule, its I-atoms, and the C-atoms beside the I-atoms respectively. The inset shows that the LUMO (isocontour: 0.0005 e Å⁻³) is a C-I σ* anti-bonding orbital of mDIB as evidenced by the nodal plane between the C- and I-atoms (black dashed lines).

The mechanism of how an electron initiates the reaction is indicated by the required bias to induce the reaction. A minimum bias of +1.1 V required for the C-I dissociation is indicative of the electronic excitation mechanism for both pathways, where the electron tunnels to an unoccupied molecular orbital forming a transient anion on the surface. This mechanistic picture is supported by the computed projected density-of-states (pDOS) for mDIB reagent. Figure 7 shows that the lowest unoccupied molecular orbital (LUMO) of mDIB is located ~0.9 eV above the Fermi level. The LUMO as shown in the inset of Figure 7 is a C-I σ* anti-bonding orbital due to the presence of a nodal plane between the C- and I-atom in both C-I bonds of mDIB. This shows that the reaction of mDIB is initiated by an electron occupying its LUMO. The average yield measured at +1.4 V is $3 \times 10^{-10}$ for the first C-I bond-breaking in the SUCCESSIVE pathway and $3 \times 10^{-12}$ for both C-I bond-breaking in the CONCERTED pathway.
Figure 8. pDOS of the chemisorbed IPh. Panel (a) shows the position of the LUMO at 1.4 eV above the Fermi level for IPh in alignment A, 1.1 eV for B, and 1.4 eV for C. The solid, dashed and dotted lines give the pDOS of the IPh adsorbate, its I-atom, and the C-atom beside the I-atom respectively. Panel (b) visualizes the LUMO (isocontour: 0.0005 e– Å–3) for all IPh configurations. All three LUMO are C–I σ* anti-bonding orbital of IPh as evidenced by the nodal plane between the C- and I-atoms (black dashed lines).

The second C–I bond-breaking in the SUCCESSIVE pathway was also found to proceed via electronic excitation. The minimum energy of electron to induce reaction for all IPh at 1.6 eV corresponds to the LUMO for all IPh around ~1.4 eV above the Fermi level as shown in Figure 8a. The LUMO of IPh as given in Figure 8b is shown to be a C–I σ* anti-bonding orbital due to the presence of a nodal plane between C- and I-atom in the C–I bond of IPh. Hence the reaction of IPh is initiated by electron occupying its LUMO.

3.2.6 Molecular dynamics

The observed electron-induced reaction was modeled using “Impulsive Two-State” (I2S) model implemented in DFT-based Molecular Dynamics (MD) calculations. Given that the observed reaction was due electron tunneling to the C–I anti-bonding orbital of the adsorbate, one electron was placed on the I-atom of the C–I bond. The system was evolved for a time (t*) on the anionic potential-energy surface (pes); The electron was removed and the system was evolved on the neutral, ground pes until the completion of the reaction. Placement of the electron in the I-atom induced C–I repulsion which initiated the reaction on the ground pes. This model has been shown to reproduce the outcomes of electron-induced surface reactions on metal27–30,39,40,54 and semiconductors.41
3.2.7 SUCCESSIVE pathway

![Diagram of SUCCESSIVE pathway](image)

**Figure 9.** Computed Impulsive Two-State (I2S) dynamics for the first C-I bond-breaking in the SUCCESSIVE pathway. Panel (a) to (c) show the time-evolution of the system from a physisorbed mDIB to give three different product alignments (A, B and C). To obtain alignment A, 0.5 e− was placed in I-atom(#1) and I-atom(#2) for \( t^* = 56 \) fs. For B, 0.8 e− was placed in I-atom(#1) and 0.2 e− in I-atom(#2) for \( t^* = 42 \) fs. For C, 1.0 e− was placed in I-atom(#1) for \( t^* = 36.5 \) fs. The green lines in all panels indicates a chemical bond from the C-dangling bond of IPh to the Cu-atom marked by green dashed circle. The blue lines show the initial C-I bond direction of the IPh, while the black lines show the instantaneous C-I bond direction of the IPh.

Three trajectories from the I2S model given in Figure 9 reproduce the observed three product alignments for the first C-I bond-breaking in the SUCCESSIVE pathway. These trajectories were obtained by partitioning the electron differently between I-atom(#1) and I-atom(#2) in mDIB. Trajectory A was obtained by equally placing 0.5 e− in both I-atom(#1) and (#2) for \( t^* = 56 \) fs. Trajectories B and C were obtained by unequal charge distributions between two I-atoms. Trajectory B was obtained by placing 0.8 e− in I-atom(#1) and 0.2 e− in I-atom(#2) for \( t^* = 42 \) fs, while trajectory C was obtained by placing 1.0 e− in I-atom(#1) for \( t^* = 36.5 \) fs. The non-integer values of added electrons used were employed to mimic the delocalization of the electron in the molecule. The short lifetimes in femtoseconds required to induce the reaction are found to be characteristic to the lifetime of anions on metal surfaces.\(^{52,53}\)
The time-evolution of trajectories A, B and C shown in Figure 9 unveils the reaction dynamics of the first C-I bond-breaking. Upon return from the anionic state, the C-I bond (#1) breaks and propels I-atom(#1) along its prior bond direction in agreement with the experiment. The C-dangling bond formed in IPh after C-I bond (#1) dissociation experiences attraction towards the nearest Cu-atom (shown as dashed green circle in Figure 9), displacing the whole IPh across the Cu-rows. The IPh then rotates in-plane in picosecond timescales until it reaches its final state. In trajectory A, as shown in Figure 9a, the IPh rotated towards the first potential well, termed A, within 1 ps. In trajectory B, as shown in Figure 9b, the IPh rotated through potential well A and reached another potential well, termed B, within 2 ps. In trajectory C, as shown in Figure 9c, the IPh rotated through potential well A and B and reached potential well, termed C, within 3 ps.

![Figure 10](image.png)

**Figure 10.** Minimum energy path between various IPh potential wells. IPh in alignments B and C were computed to be ~0.2 eV more stable than IPh in alignment A. The stabilization can be attributed to the increasingly favorable position of I-atom in IPh relative to the surface (IPh is more stable when its I-atom is located over a Cu-row). The driving force of the IPh rotation can therefore be attributed to I-Cu attraction.

The driving force of the in-plane rotation in trajectories B and C can be attributed to features on the ground pes. An approximate picture of the ground pes along the IPh rotation coordinate is given in Figure 10. The potential-energy curve shown is the minimum energy pathway between potential-wells that correspond to IPh in alignment A, B and C. Potential-well B and C were computed both to be more stable by ~0.2 eV than potential-well A. The greater stability in B and C in contrast to A can be attributed to the location of I-atom in IPh relative to the Cu-row. Potential-well B and C correspond to IPh with its I-atom adsorbed on a Cu-row, while potential-well A corresponds to IPh with its I-atom adsorbed between two Cu-rows. The driving force for the in-plane rotation in trajectory B and C can be therefore attributed to the attraction between the I-atom
in IPh and Cu-rows. This result therefore demonstrates how the Cu-rows influenced the landscape of the ground pes to induce in-plane rotation of the adsorbate. This insight has been extended to study molecular rotation on Ag(110) and Au(110).96

**Figure 11.** Computed I2S dynamics for the second C-I bond-breaking in the SUCCESSIVE pathway. Panel (a) to (c) show the time-evolution of the system from a chemisorbed IPh to give three different product alignments (A’, B’ and C’). To obtain the product alignment, 1 e− was placed in I-atom(#2) for all three IPh alignments. For alignment A’, \( t^* = 30 \) fs was used. For B’, \( t^* = 43 \) fs. For C’, \( t^* = 47 \) fs. For IPh in alignment B, the p-orbital of the C-dangling bond in IPh is pointing towards another Cu-atom on the same row marked by red circle. The green lines in all panels indicates a chemical bond from the C-dangling bond of Ph’ to the Cu-atom marked by green dashed circle.

The I2S model was also used to model the second C-I bond-breaking in the SUCCESSIVE pathway, assuming a single-electron process. The product alignment obtained in the experiment was reproduced by placing 1.0 e− in the I-atom of IPh for \( t^* = 30 \) fs in alignment A, for \( t^* = 43 \) fs in alignment B and for \( t^* = 47 \) fs in alignment C. In all the trajectories, as shown in Figure 11, C-I bond (#2) breaks and propels I-atom(#2) along its prior bond direction, in agreement with the experiment. For trajectory A’ and C’, the C-dangling bond formed in the IPh dissociation binds to the nearest Cu-atom, giving the observed final state. For trajectory B’, the ring tilts out-of-plane as C-I bond (#2) breaks, forming a C-dangling bond pointing away from the surface plane. The out-of-plane rotation of the aromatic ring is driven by C-Cu bond formation between the *anchor* C-atom and the Cu-atom underneath it (indicated by red dashed circle in Figure 11b). This particular
bond formation is not available for IPh in alignment A and C due to the misalignment between their C-atom ‘anchor’ and the underlying Cu-atom; the only C-Cu bond it can form is between the C-dangling bond from C-I bond (#2) dissociation and the nearest Cu-atom. This result demonstrates how the Cu-rows influenced the shape of the ground pes to induce out-of-plane rotation of an adsorbate.

3.2.8 CONCERTED pathway

![Diagram](image)

**Figure 12.** Computed I2S dynamics for the CONCERTED pathway. Panel (a) shows the time-evolution a physisorbed mDIB breaking both its C-I bond. The trajectory was obtained by placing 0.5 e⁻ in I-atom(#1) and I-atom(#2) for \( t^* = 57 \) fs. The green lines indicates the first C-Cu bond, while the red line indicates the second C-Cu bond. Panel (b) shows the internuclear separation between C-I(#2) and C-Cu(#2) against time. The onset of C-I bond-breaking and C-Cu bond-formation occurs at 1.2 ps.

The I2S model also reproduced the outcome for the CONCERTED pathway as shown in Figure 12a. The trajectory was obtained by placing 0.5 e⁻ charge in both I-atoms(#1) and (#2) for \( t^* = 57 \) fs. The trajectory shows that C-I bond (#1) breaks upon return from the anionic state, giving I-atom(#1) that recoils along its prior bond direction (C-I bond (#1)) and an IPh that is internally excited. The IPh breaks its C-I bond (#2) within 1.2 ps after the first bond-breaking as shown in Figure 12b. This reaction gives I-atom(#2) that recoils along its prior bond direction (C-I bond}
(2)) which has not varied significantly from its direction in the intact mDIB reagent. As the result, both I-atoms (#1) and (#2) have recoiled along their prior bond directions in the mDIB reagent due to both C-I bonds reacted within a time short compared to molecular rotation. These reaction dynamics are similar to that computed for the electron-induced reaction of diiodomethane on Cu(110), where both C-I bonds reacted within ~0.5 ps due to internal excitation of CH2I intermediate.39

3.2.9 Time-resolved dynamics

Theoretical modeling of the electron-induced reaction reveals the dependence of the reaction outcome on the lifetime of the IPh intermediate, which was long in the SUCCESSIVE pathway, and short in the CONCERTED pathway. This finding suggests the possibility of controlling the reaction dynamics by deliberately limiting the lifetime of the intermediate. The experiment would involve two time-correlated electrons where the first electron initiates the reaction, and the second electron terminates the reaction. This termination step is exemplified in the work of Rao et al where an electron was used to terminate the rotation of 2,5-dichlorothiophenol on Cu(111) at 15 K by breaking the S-H bond.97 In the context of mDIB, the first electron would dissociate the first C-I bond to initiate the IPh rotation, and the second electron would dissociate the second C-I bond to terminate the IPh rotation. If the time delay (Δt) between the initiation step and termination step is shorter than the rotational lifetime of the IPh intermediate, the extent of IPh rotation will be limited. Variation of Δt would be thus expected to alter the angular distribution between I-atoms(#1) and (#2), which can be examined by conventional STM. The time resolution of this experiment depends on what is achievable with a ‘two-pulse correlation’ scheme.98–100 Recent developments have allowed electron dosing onto a nanoscale region with femtosecond temporal resolution.101
Figure 13. Computed I2S dynamics in trajectory C in the SUCCESSIVE pathway for two-bond breaking by two time-correlated electrons. The first electron breaks the first C-I bond of mDIB; and the second electron arriving at various time-delay (Δt) can break the C-I bond of the rotating IPh. The product pattern from such experiment will be indicative of how much IPh has rotated. The computed outcome of breaking the C-I bond of IPh at Δt = 0.3 ps, 0.7 ps, 2.0 ps and 3.4 ps are shown. The green line indicates C-Cu bond. The blue line indicates the initial C-I bond direction of the IPh. The red line indicates I-atom(#2)···Ph′ angle.

This scheme has been tested in the I2S model, where the first electron breaks C-I(#1) and after a time delay of Δt, the second electron breaks C-I(#2). Figure 13 gives the predicted final states if the IPh in trajectory C of the SUCCESSIVE pathway is dissociated by a second incoming electron after Δt of 0.3 ps, 0.7 ps, 2.0 ps and 3.4 ps. The computation results clearly show increasing I-atom(#2) recoil angle from its initial direction when Δt is increased as a consequence of increasing
 extents of IPh rotation. These results imply that time-resolved reaction dynamics can be studied without the use of time-resolved STM.

3.3 Conclusions

Electron-induced reaction of mDIB physisorbed as ‘ROW’ on Cu(110) was examined by STM at 4.6 K. The reaction was initiated by one electron tunneling into the LUMO of physisorbed mDIB. Two reaction pathways were observed: SUCCESSIVE and CONCERTED. In the SUCCESSIVE pathway, one C-I bond was broken, giving an I-atom and IPh that had rotated in-plane to three different extents. This rotation was further confirmed by the observation of three different alignment of second I-atom product formed by the C-I bond-breaking of the IPh. In the CONCERTED pathway, two C-I bonds were broken, giving two I-atom found along their prior bond directions in an unrotated mDIB reagent.

Both pathways, SUCCESSIVE and CONCERTED, were reproduced in theory by the I2S model. In the SUCCESSIVE pathway, the trajectories gave significant in-plane rotation in the recoiling IPh as a result of attraction between its I-atom and the underlying anisotropic surface. The long time interval between the first and second C-I bond-breaking allowed IPh to assume various rotational lifetimes and thus extents of rotation. In the CONCERTED pathway, the time interval between the first and second C-I bond breaking was too short to allow significant IPh rotation. The dependence of the reaction outcome on the time interval between the first and second bond-breaking suggested a means to time-resolve reaction dynamics using conventional STM.
Chapter 4
Surface Anisotropy gives Bond-Selectivity

This chapter has been adapted with permission from Anggara, K. et al. Bond selectivity in electron-induced reaction due to directed recoil on an anisotropic substrate. Nat. Commun. 7, 13690 (2016) licensed under Creative Commons CC-BY 4.0. K.A. was involved in the STM experiments and conducted the ab-initio calculations.

4.1 Introduction

One of the most important quests in chemical catalysis is the search for novel strategies to selectively break or form a bond in a molecule. Central to the understanding of a catalytic mechanism is how energy in a molecule, in the presence of a catalyst, drives the system along the reaction coordinate. To this end, in heterogeneous catalysis, reaction probability is studied as a function of selective excitation in a molecule. For an excited molecule incident to a surface, the reaction has been reported to be mode-specific\(^{102–104}\), bond-selective\(^{105,106}\), and alignment-dependent\(^{107,108}\). For a molecule adsorbed on a surface, light irradiation, or electrons from Scanning Tunneling Microscopy (STM) have been reported to electronically or vibrationally excite molecule resulting in molecular translation\(^{13,15,34,35,92,109}\), rotation\(^{87–92}\), isomerization\(^{36}\) and desorption\(^{20,35,52,110}\). The dissociation of a selected bond has been demonstrated by varying the electron energy\(^{20,32,42,43}\) or, for extended adsorbates, the excitation location\(^ {43}\).

Here, we describe a high degree of bond-selectivity that has not been previously reported, originating from the directed recoil of product on an anisotropic surface. The directed recoil of a dissociation product along its prior bond has been previously reported\(^ {19,20,24,27–30,39–41,48–50}\), but its role in inducing selective reaction is observed here for the first time. We show that, for two chemically identical bonds, two different bond directions on an anisotropic surface result in hundred-fold difference in reaction probability.

The system studied was meta-diiodobenzene (mDIB) adsorbed on Cu(110); an anisotropic surface that consists of raised Cu-atom rows. The molecule was found to be physisorbed on the surface at 4.6 K with its two C-I bonds aligned differently with respect to the underlying surface: one bond directed along a Cu-row, and the other, across. Electron-induced reaction of mDIB gave
bond-selective dissociation in which the C-I bond directed along the Cu-row was a hundred-fold more likely to react than the one directed across the Cu-row. The observed bond-selective dissociation was modeled by molecular dynamics (MD) using the Impulsive Two-State (I2S) method\textsuperscript{27–30,39–41,54}. The calculations showed that the observed selectivity was due to the directed motion of the system on the anisotropic surface.

4.2 Results and discussion

4.2.1 Experiment

![Figure 1](image_url)

**Figure 1.** STM images (EXPT) and simulations (TH) of initial and final states in the bond-selective reaction of mDIB. Panel (a) shows a physisorbed mDIB in DIAGONAL configuration. The molecule has two different C-I bond directions (blue lines): C-I(AL) points along the Cu-row, while C-I(AC) points across the Cu-row. The white cross indicates the center of the mDIB STM feature. Panel (b) shows the outcome for the reaction of C-I(Al). Panel (c) shows the outcome for the reaction of C-I(AC). Each alignment has a differently rotated IPh product. Both reactions give an I-atom, and a chemisorbed IPh, both chemisorbed. In the pictured final states (PIC) for each case, the broken C-I bond is marked by blue dashed line, and the IPh binds to the Cu-atom marked by green dashed circle.

The STM images (2.5 × 1.7 nm\textsuperscript{2}) were obtained at sample bias of +0.1 V and current of 0.1 nA.
Meta-diiodobenzene (mDIB) adsorbs on Cu(110) at 4.6 K in two different geometries termed ‘ROW’ and ‘DIAGONAL’. The present chapter discusses the reaction dynamics of the latter species, ‘DIAGONAL’. Figure 1a shows the STM image (EXPT) and simulation (TH) of mDIB physisorbed in the ‘DIAGONAL’ geometry. DFT calculations show that the molecule possesses C-I bonds that point towards two different directions: C-I(AL) points along the Cu-row direction, and C-I(AC) points across the Cu-row direction (126° clockwise from [1 1 ̅ 0]). The bond lengths of C-I(AL) and C-I(AC) were computed to be ~2.1 Å, signifying that both bonds interact similarly with the surface. This adsorption geometry was also computed by Panosetti and Hofer.

To initiate the reaction, the tip was positioned on the center of mDIB STM feature (indicated by white cross in Figure 1a. Electron-induced reactions were observed when the surface bias was above +1.0 V. The reaction gave a single C-I bond-breaking, producing an I-atom and a meta-iodophenyl (IPh) in two different alignments. Comparison between STM image (EXPT) and simulation (TH and PIC) as shown in Figures 1b and 1c indicated that different C-I bonds were broken. The I-atom product was found at the four-fold hollow site adjacent to its position in the intact mDIB. The IPh product was found to bind to different surface Cu-atoms underneath the intact mDIB (green circles in Figures 1b and 1c, PIC). Figure 1b shows the major pathway where C-I(AL) was broken, and Figure 1c shows the minor pathway where C-I(AC) was broken. The large probability for C-I(AL) reaction (99.3%) as compared to C-I(AC) reaction (0.7%) clearly shows a hundred-fold preference for an electron to break C-I(AL) instead of C-I(AC) in mDIB.

Figure 2. Distance and angle distributions of the products in the bond-selective reaction of mDIB. Panel (a) shows the distribution of I-atom (black squares) and IPh (red squares) from the reaction of C-I(AL). The blue line indicates the direction of the C-I bond in the mDIB initial state. Panel (b) shows the product distribution from the reaction of C-I(AC). In all of the polar plots, the origin is the white cross (center of intact mDIB molecule), and the distance between concentric circles are 3.61 Å. All angles are measured clockwise from the [1 1 ̅ 0].
Figure 2 shows the characteristic recoil direction of the products when one of the two C-I bonds in mDIB ‘DIAGONAL’ was broken. Figure 2a shows that the I-atom and IPh products were found to recoil along the Cu-row direction in the opposite direction, consistent with the conclusion that C-I(AL) was broken. The IPh obtained when C-I(AL) broke was found to be identical to IPh in alignment B obtained from mDIB physisorbed in ‘ROW’ geometry. Figure 2b shows both products to have recoiled across the Cu-row direction, consistent with the conclusion that C-I(AC) was broken.

The strong preference for C-I(AL) bond-breaking as opposed to C-I(AC) clearly shows that the electron-induced reaction is bond-selective. Tip-induced selectivity can be ruled out as the tip was placed approximately mid-point between the two C-I bonds (white cross in Figure 1a). In a few trials, placement of the tip over C-I(AC) to induce the reaction still resulted in the breaking of C-I(AL). Given that the bond-selective in mDIB ‘DIAGONAL’ was not detected in the reaction of mDIB ‘ROW’, the origin of selectivity is concluded to be due to the adsorption geometry of ‘DIAGONAL’ on the anisotropic surface, as discussed in Theory (see below).

Figure 3. Evidence for electron-induced reaction. Reaction rate is plotted in a log-log plot against the tunneling current for the reaction of C-I(AL). The reaction rates measured at +1.3 V. Linear fit of the data points give a slope of $n = 1.1 \pm 0.2$. The error bar is the standard error of the exponential fitting of the data (see Methods for details).

Figure 3 gives the evidence that the bond-selective reaction in mDIB is initiated by tunneling electron. The reaction rates measured at +1.3 V for each tunneling current is averaged using the method established previously.\textsuperscript{31,62,111} The linear dependence between the average reaction rate and the tunneling current shows that one electron is required to initiate the bond-selective reaction. This linear relationship also rules out electric field as a cause for the reaction.\textsuperscript{23}
The relatively high bias of +1.0 V required to initiate the reaction is indicative of the electronic excitation mechanism, where an electron tunnels from the STM tip to the molecule to form a transient anion on the surface. The required bias of ~1.0 V is common to induce reactions of aryl halides on metal surfaces.

Projected density of states (pDOS) calculations as shown in Figure 4 show that the lowest unoccupied molecular orbital (LUMO) of mDIB is located 0.8 eV above the Fermi level. The inset in Figure 4 shows the LUMO to be a C-I \( \sigma^* \) anti-bonding orbital as evidenced by the nodal plane between the C- and I-atoms. Hence, the bond-selective reaction of mDIB is initiated by a tunneling electron occupying its LUMO. The yield for the major pathway was measured to be \( 9 \times 10^{-10} \) at +1.3 V. As the LUMO of mDIB is noted to be symmetric between both C-I bonds, the initial adsorption geometry alone cannot explain the origin of the bond selectivity observed in the experiment. The origin of bond selectivity can be understood in terms of the dynamics as discussed below.

### 4.2.2 Theory

The observed bond-selective reaction can be understood in terms of the recoil direction the system on the ground potential-energy surface (pes) shaped by the anistropic Cu(110) surface. The Impulsive Two-State (I2S) model implemented as molecular dynamics (MD) calculations was used to simulate the reaction. The occupation of single electron in C-I \( \sigma^* \) anti-bonding orbital of mDIB was approximated by placing an electron in the I-atom of the C-I bond. The system was then evolved on the anionic pes for a short period of time (\( t^* \)) of the order of a few femtoseconds,
and thereafter continued on the neutral, ground pes for picoseconds to observe completion of the reaction. In the present case, to ensure the breaking of C-I(AL), a full charge of 1.0 e\(^{-}\) was placed on the I-atom of C-I(AL). Similarly, to ensure the breaking of C-I(AC), 1.0 e\(^{-}\) was placed on the I-atom of C-I(AC).

**Figure 5.** Computed Impulsive Two-State (I2S) dynamics for the bond-selective reaction of mDIB. Panel (a) shows the time-evolution of C-I(AL) bond-breaking in mDIB. The trajectory was obtained by placing 1.0 e\(^{-}\) in the I-atom of C-I(AL) for \(t^* = 20\) fs. The green line in all panels indicates the chemical bond from the C-dangling bond of IPh to the Cu-atom marked by green dashed circle. Panel (b) shows the time-evolution for a trajectory where 1.0 e\(^{-}\) was placed in the I-atom of C-I(AC) for \(t^* = 20\) fs. The yellow highlights indicate that the system is in the anionic state.

Panel (a\(\prime\)) and (b\(\prime\)) shows C-I (black line), C-Cu (green line) and I-Cu (blue line) internuclear separation plotted against time. The C-Cu separation is measured from the Cu-atom nearest to the C-atom of the C-I bond: C-I(AL) in (a\(\prime\)) and C-I(AC) in (b\(\prime\)). The horizontal dotted lines mark the equilibrium separation of the indicated atomic pairs.
The experimental outcome in the major path is reproduced by the trajectory where 1.0 e\textsuperscript{−} was placed in C-I(AL) for $t^* = 20$ fs as shown in Figure 5a. The impulse obtained from the anionic pes gave C-I repulsion along the Cu-row direction which eventually resulted in C-I(AL) rupture. As shown in Figure 5a’, C-I(AL) bond rupture at $\sim 150$ fs is noted to be concurrent with C-Cu and I-Cu bond formation. In contrast, the trajectory where 1.0 e\textsuperscript{−} was placed in C-I(AC) for $t^* = 20$ fs did not result in C-I(AC) bond rupture. The failure of reaction is evident from the interatomic distance plot in Figure 5b’, where the separation between C-atom and I-atom in C-I(AC) returns to its equilibrium separation within $\sim 100$ fs.

The finding that C-I(AL) reacts more readily than C-I(AC) is in agreement with the bond selectivity observed in the experiment. The main difference between both trajectories as shown in Figure 5b’ is the initial distance between the C-atom of the C-I bond to the nearest Cu-atom. The C-Cu distance is 2.3 Å for C-I(AL) and 3.0 Å for C-I(AC). This difference between the C-Cu distances arises from the mDIB adsorption on the anistropic Cu(110) surface will be shown below to be important in inducing the bond-selective reaction.
Figure 6. Computed I2S dynamics superimposed on a restricted ground potential-energy surface (PES). The PES is constructed by varying only the two C-I bond lengths at a fixed inter-bond angle of 120°. The potential energy shown is relative to the initial state (IS). The I2S trajectory is the full molecular dynamics trajectory using all 192 atoms in the system. Panel (a) shows the I2S trajectory for 1.0 e\(^{-}\) placed in the I-atom of C-I(AL) for \(t^* = 20\) fs. Only 250 fs of the trajectory is visible within the range shown. Panel (b) shows the same for C-I(AC). The motion on the anionic PES for 20 fs is given by the yellow arrow, while the motion on the ground PES is given by the red line.

The trajectories obtained by MD calculations involving 192 atoms are superimposed on a cut on the ground pes hypersurface along the two C-I coordinates in Figure 6. The restricted ground pes shows how the potential energy varies as a function of C-I(AL) and C-I(AC) separations. In the construction of the restricted pes, all except the two aforementioned coordinates are fixed. This is a reasonable approximation as the motion in both trajectories for C-I(AL) and C-I(AC) before \(\sim 250\) fs (the portion shown in Figure 6a) mainly consists of the I-atom recoiling away from its C-atom to which it was previously bonded. The striking feature on this restricted ground pes is the difference in the reaction barriers of C-I(AL) and C-I(AC). The barrier for C-I(AL) reaction at 0.7 eV is much lower than that for C-I(AC) at 1.5 eV (beyond the range shown in Figure 6).
The success of C-I(AL) reaction and failure of C-I(AC) reaction can therefore be explained in terms of the restricted ground pes shown in Figure 6. The system is initially propelled by the impulse obtained on the anionic pes in two different directions: Along (AL) and Across (AC). In Figure 6a, the system is propelled by the impulse along the AL coordinate towards the saddle point on the restricted ground pes. The system overcomes the 0.7 eV reaction barrier, which results in C-I(AL) dissociation. On the other hand, in Figure 6b, the system is propelled by the impulse along the AC coordinate. The system fails to overcome the reaction barrier (>1.2 eV), which results in C-I(AC) staying intact. The cause of bond selectivity is therefore due to the impulse obtained on the anionic pes which propels the system towards a region on the ground pes that favors the breaking of one of the bonds.

The lower reaction barrier for C-I(AL) can be attributed to the partial stabilization given by C-Cu bond formation along the AL coordinate, which is non-existent for AC coordinate. The extent of C-Cu bond formation can be estimated from the relationship between the bond-length and bond-order (n) for atomic pairs established by Bader. At the transition state for C-I(AL), n(C-Cu) is equal to 0.5; while at the same C-I separation for AC coordinate, n(C-Cu) is equal to 0.3. Given that the energy release from C-Cu bond formation is ~3 eV, the difference in C-Cu bond order translates into ~0.6 eV greater stabilization along the AL coordinate as compared to the AC coordinate. The stabilization provided by partial C-Cu bond formation therefore accounts for the difference in reaction barriers along the AL and AC coordinates. This result demonstrates the role of anisotropic surface in providing anisotropic stabilization between reactive bonds which induces bond selectivity.
Figure 7. Minimum energy path (MEP) calculations for C-I(AL) and C-I(AC) bond-breaking. Panel (a) shows the initial, transition and final states along the MEP for C-I(AL) dissociation. The reaction barrier is computed to be 0.30 eV, while the exothermicity of the reaction is –1.20 eV. Panel (b) shows the equivalent for C-I(AC) reaction. The reaction barrier is computed be 0.19 eV, and the exothermicity, –1.30 eV. The MEP for C-I(AC) shows the molecule to have rotated in-plane before the C-I bond stretches. The MEP was calculated using Climbing-Image Nudged Elastic Band (CI-NEB) method (see Methods for details).

The reaction barriers along the AL and AC coordinates are qualitatively reversed if the reaction proceeds thermally through the minimum energy pathway (MEP). As shown in Figure 7, the barrier for C-I(AL) reaction ($E_a = 0.3$ eV) was computed to be higher than that for C-I(AC) ($E_a = 0.2$ eV). The result suggests that bond-selectivity may still be observed but with the opposite outcome to that observed by electron-induced reaction. The reported bond-selectivity in the electron-induced reaction is therefore found to be unique to the impulsive dynamics – here defined as the directed recoil of atoms due to sudden anion formation. This raised the possibility of utilizing electrons, instead of thermal energy, to access new bond-selective pathways for a catalytic system.

### 4.3 Conclusions

A high degree of bond-selectivity was reported for the reaction of mDIB on Cu(110) at 4.6 K. The C-I bond directed along the Cu-row was found to react with a 99/1 ratio relative to that of the C-I bond directed across the Cu-row. The origin of the selectivity is the directed recoil on the
anisotropic surface. The anisotropic substrate and the adsorption geometry give rise to two different proximities of a C-I bond to the nearest Cu-atom, leading to a greater stabilization and hence lower barrier in the breaking of the C-I bond more closely adjacent to a Cu-atom. Significantly this hundred-fold selectivity was observed despite both bonds having the same chemical identity. Directed recoil on anisotropic surface can induce bond-selectivity that is not observed thermally. This work may provide a basis for the understanding of other electron-induced reactions, such as those involved in photocatalytic systems. ¹¹³,¹¹⁴
5.1 Introduction

Bimolecular reaction is fundamental to reaction dynamics. Bimolecular dynamics was first studied in the gas-phase by crossed molecular beams and by infrared chemiluminescence. Crossed beams of alkali metals + halide gave evidence of ‘forward’ scattering of one product along the incoming beam direction, and ‘backward’ of the other product, this being also subsequently observed for F + H$_2$. While both methods illuminated the reaction dynamics, both suffered from full averaging over impact parameter and angle of approach, which obscured the steric requirement for reaction. This led to the field of stereodynamics which aimed to control the collision geometry. Partial control was achieved by aligning the reagent using an electric field, by using polarized laser pulses, and by inducing reaction in Van der Waals complexes.

The alignment of reagents can also be achieved by their adsorption at a surface, where the relative position and orientation between the adsorbed molecules can be determined by single-molecule detection techniques, prominently Scanning Tunneling Microscopy (STM). Surface-aligned molecules opened the way to the study of Surface-Aligned Reaction (SAR) with controlled reagent geometries. Reaction was initiated by photon-induced or electron-induced formation of a reactive atom or radical aimed in the direction of some stationary target. To ensure that the target remained stationary prior to the collision, the projectile excitation was made local employing the tip of an STM. This SAR experimental scheme enabled the study of bimolecular reactions one-collision-at-a-time with some control over collision geometry. This control of collision geometry was rendered imperfect by scattering of the atom or radical (here designated the ‘projectile’) as it traversed the surface. Such problem has been shown to be remedied by reducing the separation between reagent pairs by self-assembly or tip manipulation.

To reduce the uncertainty in the collision geometry, the projectile in an SAR experiment would need to be propelled consistently in a specific direction. Direction of motion has previously been shown to be influenced by the surface state for a physisorbed projectile, or more generally by
directed recoil along a prior bond direction\textsuperscript{19,20,24,27–30,39–41,48–50}. However, deflection of the projectile from its initial path is still likely to occur due to scattering by atoms of the underlying surface. Here we address this problem by using surface atoms to collimate the recoiling species, in a manner analogous to the use of slits in a gas-phase molecular beam apparatus. We shall show that a recoiling, hence translationally ‘hot’, CF\textsubscript{2} radical preferentially recoils unidirectionally along a row of Cu-atoms in an underlying surface, Cu(110). The CF\textsubscript{2} adsorbate beam is sharply collimated due to its chemisorptive attraction to successive Cu-atoms of single prominent atomic rows directed along [1\overline{1}0] axis of Cu(110). These ‘surface-molecular-beams’ are found, in the present instance, to extend for distances of up to 50 Å.

The existence of the surface-molecular-beams provides a new tool for the study of molecular scattering, either inelastic or reactive. In the present instance it appears neither necessary nor advantageous to study scattering at a beam crossing-point, as has been so instructive in gases. Instead we use the highly collimated recoiling species comprising the ‘surface-molecular-beam’ as the ‘projectile’, and a stationary adsorbate atom or radical as the ‘target’. In contrast to the beam + beam scattering studied heretofore, the fixed nature of the chemisorbed target enables the study of individual projectile-target collisions with selected ‘impact parameter’ (this being the perpendicular ‘miss-distance’ between the projectile and its target). In the present introductory study we shall give experimental examples of reactive and non-reactive inelastic scattering collisions, in both of which the impact parameter is controlled to better than 1\% accuracy.

The impulse along the beam direction in the present work stemmed, from electron attachment, interpreted, as before, in terms of an ‘Impulsive Two-State’ (I2S) model\textsuperscript{27–30,39–41,54}. The novelty is that the recoiling species, CF\textsubscript{2}, exhibited motion carrying it accurately unidirectionally along a row of copper atoms. The process of successive binding with the row-atoms will be shown (below) by Molecular Dynamics (MD) analysis to be a regular alternation of C-atom chemical binding causing frustrated rotation, followed by frustrated translation. The combination of motions operates over-all like a ‘ratchet’ in which the C-atom binds chemically in succession to adjacent Cu-atoms of a single row, and after each such chemical binding event, the heavy F-atoms move to stabilize the newly formed C-Cu bond, shifting the CF\textsubscript{2} further along the same direction as before but in frustrated translation. This alternation of rotation with translation is that envisaged by the earlier authors.\textsuperscript{13,137–141} The energy-loss per ratcheting event is sufficiently small that CF\textsubscript{2} is observed to travel along a line of up to ~20 Cu-atoms, a distance of ~50 Å. The observation of
these new ‘surface-molecular-beams’ permits the CF$_2$ projectile in the present work to be aimed at selected adsorbate targets, with known impact parameter depending on the location of the fixed target, and variable collision energy depending on the CF$_2$ travel distance to that target.

The CF$_2$ projectile was formed from the C-F bond-breaking in a CF$_3$ chemisorbed on Cu(110) at 4.6 K by attachment of a single electron. This electron-induced reaction selectively broke the C-F bond directed along a Cu-row, giving an F-atom and a CF$_2$ as the products. The CF$_2$ product was found to recoil long-distances unidirectionally along the Cu-row with a very narrow ($\pm 1^\circ$) angular distribution. In this Chapter, the directed CF$_2$ projectile was aimed, with a known impact parameter at a chemisorbed stationary CF$_2$ target, to study the molecular motions in the bimolecular CF$_2$ + CF$_2$ association reaction leading to C$_2$F$_4$ formation. When aimed at a chemisorbed I-atom, it could be used to examine the scattering in a CF$_2$ + I inelastic encounter, at a known impact parameter (see Appendix A).

The CF$_2$ + CF$_2$ encounter, which was the most studied, was examined as a function of impact parameter and collision energy. The impact parameter ($b$) was varied by aiming the CF$_2$ projectile towards the CF$_2$ target chemisorbed on the same Cu-row ($b = 0$ Å), or alternatively on an immediately adjacent Cu-row ($b = 3.6$ Å). The CF$_2$ + CF$_2$ collision with $b = 0$ Å was found to result in association reaction, giving a chemisorbed C$_2$F$_4$. In contrast, the collision with $b = 3.6$ Å resulted in visible momentum transfer to the target CF$_2$ but no C$_2$F$_4$ product formation. Examination of the corresponding MD indicates that the $b = 0$ Å requirement of the association reaction stemmed from the need to bring both CF$_2$ to its closest approach distance with the CF$_2$ projectile and CF$_2$ target adsorbed on adjacent short-bridge sites of a Cu-row. This geometry allowed the C dangling-bond of the projectile CF$_2$ to overlap significantly with that of the CF$_2$ target to form a C-C sigma bond.

The collision with $b = 0$ Å was studied as a function of collision energy ($E_{\text{col}}$) by varying the recoil distance of the CF$_2$ projectile prior to its collision with the CF$_2$ target. Theory showed, as expected, that the larger the recoil distance ($d_{\text{rec}}$) prior to collision with the target, the more of its translation energy and its rotation energy had been lost to the surface, resulting in a lower collision energy $E_{\text{col}}$. At small $d_{\text{rec}}$, collision with high $E_{\text{col}}$ the C$_2$F$_4$ was observed to recoil ‘forward’, i.e. further along the direction of the incoming CF$_2$ projectile. By contrast, at large $d_{\text{rec}}$, with low $E_{\text{col}}$ C$_2$F$_4$ was found to recoil ‘backward’, along the direction from which the CF$_2$ projectile had come.
This clear control over the surface reaction dynamics stems from the presence on the surface of reagent beams with variable translational energy but with a consistent well-defined collision coordinate. Definitive control of the reaction dynamics is a consequence, therefore, of the novel circumstance of bimolecular reaction between a pair of projectile and target \textit{CF}_2 collision-partners both located in a single surface molecular-beam. Equally well-defined dynamics can be anticipated for cases in which the projectile and target are in different, but determined, surface-molecular-beams, a situation encountered later in the present study.

The computed trajectory for the ‘forward’ pathway showed that the projectile reacted with the target at its first collision, giving forward scattered \textit{C}_2\text{F}_4 that retained translation energy from the projectile. Examination of the collision dynamics for association to form the forward scattered \textit{C}_2\text{F}_4 showed that a translation energy of 0.3 eV was required to bring the system to a close-approach centre-of-mass separation of \~2.6 \AA\ (~1 unit cell). From this configuration out-of-plane rotation of the projectile with \( \geq 0.6 \) eV of rotation energy stretched the bond of the \textit{CF}_2 to the \textit{Cu}-surface, and directed this projectile dangling bond towards the target C-atom to initiate the formation of the new C-C bond.

In the computed ‘backward’ trajectory, MD calculations showed that the projectile failed to react with the target at its first collision. The \textit{C}_2\text{F}_4 product was formed only after a secondary collision between the projectile and the target, catalyzed by a raised \textit{Cu}-atom.
5.2 Results and discussion

5.2.1 Electron-induced reaction of CF₃: Experiment

Figure 1. Large-scale STM image (30.0 × 30.0 nm²) of Cu(110) surface at 4.6 K after dosing with CF₃I. The surface temperature rose up to ~14 K during the dose. The CF₃I molecules were observed to dissociate upon adsorption, giving pairs of I-atom (bright circular feature) and CF₃ (dim oval feature surrounded by a depression), both chemisorbed. A pair is indicated by two dashed circles in the Figure. The STM image was obtained at sample bias of −0.1 V and current of 0.5 nA.

The precursor for both the difluorocarbene (CF₂) projectile and the CF₂ target on Cu(110) at 4.6 K was chemisorbed trifluoromethyl (CF₃) which was generated by dosing iodotrifluoromethane (CF₃I) onto the surface. The CF₃I molecule was found to dissociate its C-I bond upon adsorption, giving a chemisorbed pair of CF₃ and I-atoms as shown in Figure 1. Given that the surface temperature rose only by ~14 K during the dose, the most likely cause for the dissociation is electron-transfer from the surface to the molecule, similar to the case of diiodomethane on Cu(110).³⁹
Figure 2. STM images (EXPT) and simulations (TH) of initial and final states in the electron-induced reaction of a CF$_3$ to give a CF$_2$ and an F-atom. Panel (a) shows the CF$_3$ adsorbed with one of its C-F bonds pointing along the Cu-row, this bond being termed C-F(AL) (grey dashed line). The white cross indicates the center of the STM feature of the intact CF$_3$ reagent. Panel (b) shows the final state of the reaction, addition of an electron has broken C-F(AL), giving a CF$_2$ and an F-atom. The STM images (2.3 × 2.7 nm$^2$) were obtained at sample bias of −0.1 V and current of 0.3 nA.

As shown in Figure 2a (EXPT), chemisorbed CF$_3$ was imaged as an oval elongated in the direction across the Cu-row with an apparent height of 0.07 ± 0.04 Å surrounded by a depression. DFT calculations show that CF$_3$ is adsorbed on a Cu-row, bonded atop a Cu-atom via its C-atom with $E_{\text{ads}} = 2.53$ eV. In the computed structure, the C-F bond directed along the Cu-row direction, termed C-F(AL), was elongated by ~4% in comparison with the two other C-F bonds. This elongation implies that C-F(AL) bond is slightly weakened relative to the other two C-F bonds, as a consequence of molecular chemisorption.
Electron-induced reaction of the chemisorbed CF$_3$ was observed at a bias of above +0.9 V. The reaction broke a single C-F bond, giving an F-atom and a CF$_2$ as reaction products as shown on Figure 2b. Based on the product recoil along the Cu-row, the reaction was found to selectively break C-F(AL) in qualitative agreement with the earlier finding that this anisotropic surface induces bond-selective reaction.$^{142}$ The CF$_2$ product was imaged as an oval with apparent depth of 0.23 ± 0.04 Å, surrounded by a depression. The F-atom product was imaged as a circular depression with apparent depth of 0.36 ± 0.04 Å. Both species, CF$_2$ and F, were observed to adsorb at short-bridge sites between two Cu-atoms along the Cu-row direction, in agreement with the most stable adsorption geometries calculated by DFT. The adsorption energy was computed to be 1.89 eV for the chemisorbed CF$_2$, and much greater, 5.01 eV, for the chemisorbed F-atom. This difference in adsorption energy is due to covalent bonding for CF$_2$, as distinct from the stronger ionic bonding for F (see Appendix B for details).

![Figure 3](image)

**Figure 3.** Distributions of CF$_2$-radical and F-atom products from electron-induced dissociation of CF$_3$. Panel (a) shows distance and angle distribution for CF$_2$ (red squares) and F-atom (green squares). The CF$_2$ was found to recoil along a single Cu-row ($\theta = 0 \pm 1^\circ$) opposite to the direction of the prior C-F(AL) bond (broken line). The colored ticks on the perimeter of the circle give the average recoil direction of the products (red for CF$_2$, green for F). The
The origin of the polar plot is at the white cross which indicates the center of the intact CF$_3$ reagent. The data have been folded such that the observed CF$_2$ is shown in the upper-half of the polar plot. The distance between concentric circles is 10 Å. Panel (b) gives the distance-distribution for the CF$_2$ recoil along the Cu-row (bin size: 2.55 Å). The error bars represent the standard error (square root of the number of events).

The most striking feature in the electron-induced dissociation of chemisorbed CF$_3$ is the markedly directional-recoil of the CF$_2$ at 0 degrees along the Cu-row direction, as shown in Figure 3a. The product CF$_2$ was found to recoil long distance ($\langle d_{\text{CF}_2} \rangle = 19.7 \pm 7.8$ Å, see Figure 3b for the distance distribution) unidirectionally along a single Cu-row ($\langle \theta_{\text{CF}_2} \rangle = 0 \pm 1^\circ$). The recoil of CF$_2$ along the Cu-row was consistent with the notion that C-F(AL) (direction shown as dashed line in Figure 3a) was the bond broken in the reaction. The strong unidirectionality of recoil is consistent with the observation in molecular dynamics (MD) calculations (see below) that the Cu-row acts as a guide to the CF$_2$. We show, below, how this guide operates by way of consecutive bond-formation to the atoms of the Cu-row. Stated more generally, this finding shows that features on an anisotropic surface can constrain the motion of a ‘hot’ adsorbate, much as a railway track guides a train. Earlier studies from this laboratory were designated ‘SAR’, for ‘Surface-Aligned Reaction’; here the high degree of reagent directionality invites the description: ‘1D-SAR’.

The recoil direction of the F-atoms was found to be opposite to that of CF$_2$, (forward for CF$_2$, backward for F) as for pairs of products of electron-induced reaction in other molecules.\textsuperscript{19,20,24,27–30,39–41,48–50} On the basis of its low mass (19 amu compared with 50 amu for CF$_2$) the F-atom might be expected to recoil further than CF$_2$. However, this is not the case; CF$_2$ recoils much further than F ($\langle d_F \rangle = 3.8 \pm 0.7$ Å, compared with $\langle d_{\text{CF}_2} \rangle = 19.7 \pm 7.8$ Å). As will be explained in detail, the CF$_2$ motion has a specific cause, taking place by successive chemisorption events along the rows of Cu-atoms on the surface. By contrast the F-atoms, with strong surface-binding (5.01 eV), exhibit highly inelastic surface-interaction. MD calculations predict that a small misalignment of the C-F(AL) bond along the [1\(\bar{1}\)0] direction of Cu(110), namely a deviation of $< 7^\circ$ away from the Cu-row, can account for the observed spread of chemisorbed F-atom product, at angles: $\pm 71^\circ$, $\pm 110^\circ$ and $179^\circ (\pm 10^\circ)$ (all relative to the Cu-row direction).
Figure 4. Evidence for single-electron reaction. Linear fit of the data (red line) in the log-log plot of reaction rate against tunneling current gives a slope of $n = 0.8 \pm 0.2$ – indicating the C-F bond-breaking in CF$_3$ is a one-electron process. The reaction rates were measured at +1.3 V. The error bars represent the standard error of the exponential fitting of the data (see Methods for analysis details).

The evidence for the nature of the electron-induced reaction is given by the measurement of reaction rate as a function of the tunneling current. The single-molecule reaction rate was measured at +1.3 V using the previously established method$^{31,62}$. As shown in Figure 4, the linear dependence between the reaction rate and the current indicated that one electron was required to induce the reaction of CF$_3$. This linear dependence also excludes electric field as the cause of reaction.$^{23}$

Figure 5. Projected density-of-states (pDOS) of the chemisorbed CF$_3$. The pDOS of chemisorbed CF$_3$ (black line) shows a CF$_3$-Cu hybrid state peaked at 1.3 eV above the Fermi level. The inset visualizes this hybrid state (isocontour: 0.00015 e$^{-}$Å$^{-3}$), showing a nodal plane (dashed line in inset) between C-atom and F-atom in C-F(AL). The red line gives the projection of CF$_3$ $\sigma^*$ molecular orbital in the gas phase onto the pDOS of CF$_3$ on the surface (see Methods for projection details). The result shows that the 1.3 eV hybrid state is the first unoccupied state that has a C-F $\sigma^*$ anti-bonding character.
The mechanism of the electron-induced reaction of CF\textsubscript{3} is indicated by the minimum bias required to induce the reaction at +0.9 V. Projected density-of-states (pDOS) calculations of the chemisorbed CF\textsubscript{3} given as the black curve in Figure 5 show the existence of a CF\textsubscript{3}-Cu hybrid state at 1.3 eV above the Fermi level whose onset at ~0.7 eV is in agreement with the observed threshold. The reaction of CF\textsubscript{3} is thought to be induced via electronic excitation to form a short-lived CF\textsubscript{3} anion by single-electron occupancy of the CF\textsubscript{3}-Cu hybrid state. The yield of this process was measured to be 8.8 × 10\textsuperscript{-12} at +1.3 V. Given that the survival probability of an anion on a metal surface decreases exponentially with respect to the lifetime\textsuperscript{52,53,143}, the low yield is due at least in part to the extended lifetime (tens of femtoseconds – see the following section) required to break the C-F bond in CF\textsubscript{3}.

The character of this hybrid state is examined by visualization in real-space, as shown in the inset of Figure 5. The presence of nodal plane between the C-atom and the F-atom in the C-F bond suggests that the hybrid state possesses a C-F $\sigma^*$ anti-bonding character. This $\sigma^*$ character of the hybrid state was further examined by projecting the adsorbate pDOS onto its C-F $\sigma^*$ anti-bonding molecular orbital (MO) following the procedure established by Lorente et al.\textsuperscript{78,79} In the present system, a C-F $\sigma^*$ anti-bonding MO of a CF\textsubscript{3} in the gas-phase distorted to its chemisorbed geometry was projected onto the pDOS of CF\textsubscript{3} chemisorbed on the surface. The result of this projection is given by the red curve in Figure 5 which reveals the extent of C-F $\sigma^*$ anti-bonding character for all electronic states in the chemisorbed CF\textsubscript{3}. The non-zero value of this projection for the hybrid state at 1.3 eV above the Fermi level shows that this state is the lowest unoccupied electronic state of the chemisorbed CF\textsubscript{3} that possesses a C-F $\sigma^*$ anti-bonding character.

5.2.2 Electron-induced reaction of CF\textsubscript{3}: Theory

The Impulsive Two-State (I2S) model was employed to interpret the electron-induced reaction of CF\textsubscript{3}. The electron occupation in the state possessing C-F $\sigma^*$ anti-bonding character was simulated by placing a single electron in the F-atom of C-F(AL) with the aid of a pseudopotential (see Methods). The system was evolved on this anionic potential-energy surface for a period of femtoseconds ($t^*$) required for subsequent reaction on the ground potential-energy surface with the observed product recoil distances.
Figure 6. Computed ‘Impulsive Two-State’ (I2S) dynamics for the reaction of CF$_3$. The long-range recoil of CF$_2$ is obtained by placing an electron in the F-atom of the C-F(AL) for $t^* = 13$ fs. F-atoms are green and C-atoms black. The impulse (red explosion at $t = 0$ fs) propels CF$_2$ and F in opposite directions along the prior C-F(AL) bond-direction. The CF$_2$ ‘ratchets’ along the Cu-row for 8 cycles before stopping 8.5 unit cells (21.7 Å) away from the initial position (see below for detailed analysis of the ‘ratcheting’ dynamics). The trajectory exemplifies the case that corresponds to the average distance traveled by the CF$_2$ in the experiment.

Figure 6 shows a trajectory from the I2S model that reproduces the average recoil distance of the CF$_2$ observed in the experiment. Placement of an electron in C-F(AL) for $t^* = 13$ fs gave a repulsion between the C- and F-atom of the C-F(AL) bond, which propelled the CF$_2$ and the F-atom along the Cu-row in opposite directions for the requisite distances. The F recoiled only a short distance due to strong binding to the Cu-surface, whereas the CF$_2$ exhibited long-range linear recoil along the Cu-row, as found experimentally and as modeled by MD calculations below.

The ability to measure the recoil distance is specific to the employment of STM as in the present study. Relevant earlier work has been concerned with measurement of the average diffusion distance of CO across metal surfaces, induced by pulsed laser irradiation. The translation-rotation coupling in the adsorbate was proposed as an essential step in causing the observed CO diffusion in these earlier works. The detailed dynamics for long-range CF$_2$ diffusion, reported here for the first time, are in general accord with this earlier proposal. Efficient mode-
coupling is required to explain the observation that a single impulse (here from a single incident electron) can cause a CF$_2$ radical to recoil a measured distance of up to 50 Å.

**Figure 7.** Ratcheting dynamics of the recoiling CF$_2$ along the Cu-row in the I$_2$S trajectory. The ratchet motion consists of two alternating motion: (a) the C-atom of CF$_2$ binding to successive Cu-atoms of a row, and (b) the two heavy F-atoms moving forward with respect to the fixed chemisorbed C-atom. The red dashed line represents the C-Cu bond whose formation serves as the driving force of the motion. The vertical dashed black lines in (a) and (b) gives the positions of Cu-atoms along the Cu-row. Panel (c) shows the alternating translation energy of F-atoms (green) and C-atom (black) in the recoiling CF$_2$ moving from left to right along the first five atoms of a Cu-row (this motion persists experimentally for up to ~20 Cu-atoms of a row).

Efficient translation-to-rotation energy transfer would be consistent with the observed motion, competing favorably with energy loss to the surface. As shown in Figure 7, our MD calculation for CF$_2$ give evidence of a multiple succession of pairs of frustrated rotation followed by frustrated translation impulses carrying the CF$_2$ for long distances. Figure 7a shows a chemisorptive frustrated (i.e. partial) rotation event. This partial CF$_2$ rotation carries the C-atom from left to right in the Figure (see Panel 1 to 3 in Figure 7a), extending an existing C-Cu bond and forming a new one at the adjacent Cu-atom of the same Cu-row. This was identified in previous work as ‘concerted reaction’ responsible for localization of the reaction product (‘LAR’, Localized Atomic Reaction$^{19,28,49}$); in the present case the reaction is localized to the successive Cu-atoms of a row. From the electronic structure perspective, the frustrated rotation (from Panel 1 to 2 in Figure 7a)
maximizes the CF₂ bonding to a pair of adjacent Cu-atoms of the row (see Appendix B). In Figure 7b, the center-of-mass of CF₂ moves further along the same direction, from left to right in the Figure (see Panel 3 to 5 in Figure 7b), as the heavy F-atoms at the CF₂ center-of-mass swing around the fixed point of the chemisorbed C; this constitutes the frustrated translation. The frustrated translation is caused by the C-atom to approach the Cu-atom below (in going from Panel 3 to 4 in Figure 7b), giving a torque which results in forward motion of the F-atoms of CF₂. Figure 7c shows the alternating motion of C and then F in CF₂ as frustrated rotation gives way to frustrated translation. In Figure 6 we characterized this motion as ‘ratcheting’. The claw of the ratchet that initially grips the surface is C. The attached tail of the ratchet follows the claw; it is the two heavy F-atoms. Since the claw engages with successive Cu-atoms of a single row, the ratchet operates unidirectionally. This successive bonding to Cu-atoms by the CF₂ is caused by its directional interaction with the surface since the C-atom p-orbital (i.e. LUMO of CF₂, see Appendix B) is parallel to the Cu-row direction.

Figure 8. Time evolution of translational energy of CF₂ (red line) and F-atom (green line) along the Cu-row in the I2S trajectory. The translation energy of F-atom first crosses zero at 79 fs, for CF₂, 1929 fs. The dashed green line corresponds to the oscillation of F-atom between two binding sites located mid-point between two adjacent Cu-atoms. This result highlights the stark difference in energy dissipation rate to the surface between a molecule and an atom.

The effect of the translation-rotation coupling described above for CF₂, but absent in a single F-atom, is evident from the time-evolution of their respective translation energies. As shown in Figure 8, the F-atom loses all its energy as early as 79 fs, but the CF₂, cools as late as almost 2 ps due to facile internal energy-transfer in the polyatomic species. The slow cooling of CF₂ with increasing recoil distance, as shown in Figure 9 below, permits study of the effect of collision energy (E_{col}), which consists of translational energy (E_{TRANS}) and rotational energy (E_{ROT}), on the outcome of a Surface-Aligned Reaction (SAR). In the 1D-SAR studied in the next section, the CF₂ + CF₂ collision with low E_{col} was obtained using a long recoil distance of the projectile prior to
collision with the target. Conversely, high $E_{\text{col}}$ could be achieved using a short recoil distance of the projectile.

Figure 9. Computed distance-evolution of the translation energy ($E_{\text{TRANS}}$) and rotation energy ($E_{\text{ROT}}$) in a CF$_2$ recoiling along the Cu-row direction in the I2S trajectory. The translation energy along the direction of the Cu-row is given by the red line. The black line gives the energy of the frustrated rotation in the ‘ratchet’ dynamics.

5.2.3 Surface-aligned reaction of CF$_2$ + CF$_2$: Experiment
Figure 10. STM images (EXPT) of the bimolecular CF$_2$ + CF$_2$ association reaction on a single Cu-row. Panel (a) shows the CF$_3$ and the CF$_2$ target adsorbed on the same Cu-row. The white cross indicates the position where the tip was placed to generate the CF$_2$ projectile from the CF$_3$. The white arrow indicates the recoil direction of the CF$_2$ projectile along the Cu-row towards the CF$_2$ target. Panel (b) shows the C$_2$F$_4$ product formed on the same Cu-row as in (a) as a result of collision between the CF$_2$ projectile and the CF$_2$ target. The STM images (3.5 × 4.6 nm$^2$) were obtained at sample bias of −0.05 V and current of 0.05 nA.

Here we demonstrate a 1D-SAR experiment between a projectile CF$_2$ and a target CF$_2$ along a single Cu-row, a one dimensional event. As shown in Figure 10a, the initial state consists of a chemisorbed CF$_3$, the precursor for the CF$_2$ projectile that will travel along a single Cu-row to a stationary CF$_2$ target on the same row. The reaction was initiated electronically by placing the tip over the chemisorbed CF$_3$ to form the recoiling CF$_2$ projectile. The final state of the CF$_2$ + CF$_2$ reaction consists of a tetrafluoroethylene (C$_2$F$_4$) and an F-atom, as shown in Figure 10b. The reaction took place by a two-step process: (i) the electron-induced reaction of the chemisorbed CF$_3$ produced a recoiling CF$_2$ projectile along the Cu-row, and (ii) the CF$_2$ projectile collided with the stationary CF$_2$ target, chemisorbed on the same row, to form a C$_2$F$_4$. This C$_2$F$_4$ product, as shown in Figure 10b, was imaged as an oval protrusion elongated across the Cu-row direction, with an apparent height of 0.29 ± 0.04 Å, centered above a Cu-atom (atop site). Further electron pulses on the C$_2$F$_4$ product gave evidence that the product was a single, chemisorbed C$_2$F$_4$ molecule, as discussed below.

Figure 11. STM images (EXPT) of the electron-induced diffusion of an intact C$_2$F$_4$ along a single Cu-row. Panel (a) shows the STM image of a C$_2$F$_4$ on a Cu-row (white dashed line). The white cross defines (i) the center of C$_2$F$_4$ STM feature and also (ii) the position where the tip was placed to induce the diffusion. Panel (b) shows the C$_2$F$_4$
following diffusion along the same Cu-row (along the white dashed line), evidencing that the C$_2$F$_4$ is a single molecule. The STM images (2.6 × 3.2 nm$^2$) were obtained at sample bias of −0.05 V and current of 0.05 nA.

The evidence that the C$_2$F$_4$ product from the CF$_2$ + CF$_2$ 1D-SAR is a single molecule is given by the C$_2$F$_4$ electron-induced diffusion shown in Figure 11. A tunneling electron at a bias of +1.3 V was found to diffuse the C$_2$F$_4$ as far as ~16 Å (~6 unit cells) from its initial atop binding site, to another atop site along a single Cu-row. This observed diffusion is consistent with the notion that a C-C covalent bond has been formed between the CF$_2$ projectile and the CF$_2$ target, so that the C$_2$F$_4$ diffuses as a single object for a considerable distance. Hence, we have shown that a CF$_2$ + CF$_2$ collision resulted in an association reaction, producing a single C$_2$F$_4$. This C$_2$F$_4$ was computed to be chemisorbed above a Cu-atom with its C-C bond aligned along the Cu-row direction (see Figure 12a, Panel TH, or Appendix B), parallel to the line joining the CF$_2$ projectile and the CF$_2$ target.

Figure 12. STM images (EXPT) and simulation (TH) of the electron-induced conversion of a chemisorbed C$_2$F$_4$ to a physisorbed C$_2$F$_4$. Panel (a) shows the chemisorbed C$_2$F$_4$. The white cross defines the position where the tip was placed to induce the process. Panel (b) shows the physisorbed C$_2$F$_4$. This conversion evidences that the CF$_2$ + CF$_2$ association reaction gives a single, chemisorbed C$_2$F$_4$. The STM images (2.5 × 2.5 nm$^2$) were obtained at sample bias of −0.05 V and current of 0.05 nA.
Tunneling electrons at +1.3 V were also found to convert the chemisorbed C$_2$F$_4$ into another adsorption state shown in Figure 12, possibly due to electron-induced dissociation of covalent C-Cu bonds in the chemisorbed C$_2$F$_4$. This new C$_2$F$_4$ state, shown in Figure 12b, was imaged as a circular protrusion with an apparent height of 0.81 ± 0.04 Å. DFT calculations show that this process can be attributed to the conversion of a chemisorbed C$_2$F$_4$ to a physisorbed C$_2$F$_4$. The computed physisorbed C$_2$F$_4$ ($E_{\text{ads}} = 0.40$ eV) has all its C-F bonds pointing parallel to the surface, and a C-C bond distance of 1.34 Å, similar to the experimental C-C bond length in a gaseous C$_2$F$_4$ at 1.31 Å (ref 144). The chemisorbed C$_2$F$_4$ ($E_{\text{ads}} = 0.51$ eV) had all its C-F bonds pointing away from the surface, and a computed C-C bond distance of 1.47 Å, longer than that in the physisorbed C$_2$F$_4$. Hence, in the chemisorbed molecule, the C-C bond is a single bond (since the other C bond attaches the molecule to the surface – see Appendix B); in the physisorbed C$_2$F$_4$, the C-C bond is a double bond. The observation of the C-I bond dissociation in CF$_3$I, the C-F bond dissociation in CF$_3$, the CF$_2$ + CF$_2$ association reaction, and the conversion of a chemisorbed C$_2$F$_4$ into a physisorbed C$_2$F$_4$, thereby provide a complete mechanistic picture of C$_2$F$_4$ generation from a CF$_3$I-dosed metal surface. The present work may provide clues to the different nature of the reactions observed in temperature programmed desorption studies of CF$_3$I dosed onto various metal surfaces.$^{145–148}$

More information, not available by other techniques, concerning the reaction dynamics of the CF$_2$ + CF$_2$ association can be obtained by examining the outcome of CF$_2$ + CF$_2$ collision as a function of impact parameter ($b$) as well as collision energy ($E_{\text{col}}$). The steric requirement of the association reaction is made evident by examining the collision outcome as a function of $b$. This parameter can be varied by placing the CF$_2$ target on either the same or a different Cu-row than the CF$_2$ projectile. Furthermore the topography of the CF$_2$ + CF$_2$ potential-energy surface can be explored by examining the collision outcome as a function of $E_{\text{col}}$. This parameter can be varied by altering the recoil distance of the CF$_2$ projectile prior to its collision with the CF$_2$ target. As shown in Figure 9 above, $E_{\text{col}}$, which consists of the CF$_2$ projectile translational ($E_{\text{TRANS}}$) and rotational energy ($E_{\text{ROT}}$), decreases as the projectile recoil distance is increased.
Figure 13. STM images (EXPT) of the CF$_2$ + CF$_2$ abortive reaction due to collision at a selected $b = 3.6$ Å. Panels (a) and (b) show the initial and final states of the abortive reaction. The white cross in (a) and (b) indicates the position where the tip was placed to generate the CF$_2$ projectile from the CF$_3$. The white solid arrow in (a) and dashed arrow in (b) indicate the recoil distance and direction of the CF$_2$ projectile. The black arrow in (b) indicates the recoil distance and direction of the CF$_2$ target from its initial position (black cross) along from the projectile approach direction. The STM images ($2.1 \times 4.7$ nm$^2$) were obtained at sample bias of $-0.05$ V and current of 0.05 nA.

The effect of varying the impact parameter is shown in Figure 10, where CF$_2$ + CF$_2$ collision with $b = 0$ Å gives association reaction, and in Figure 13, where CF$_2$ + CF$_2$ collision with $b = 3.6$ Å gives abortive reaction. The abortive reaction here is defined as an outcome where momentum is transferred from the CF$_2$ projectile to the CF$_2$ target without concurrent C$_2$F$_4$ formation. The CF$_2$ target was found to be repelled a substantial distance, $<d> = 13.5 \pm 3.3$ Å, along the continuation of the approach direction of the colliding projectile. The evidence indicates that a CF$_2$ + CF$_2$ collision with $b \sim 0$ Å is a requirement for the association reaction.
The MD calculations, below, show that the propulsion of the projectile towards the target with $b = 0$ Å brings the CF$_2$ to a center-of-mass separation of 2.6 Å (~1 unit cell), where both CF$_2$ are adsorbed on adjacent short-bridge sites of the same Cu-row. This configuration, shown by the trajectory to be that from which the new carbon-carbon bond formation begins, allows the C-dangling bond orbitals in both CF$_2$ to overlap and form a C-C sigma-bond. Achieving this configuration is a requirement for association reaction in which the CF$_2$ projectile moves toward the CF$_2$ target with $b = 0$ Å and also with a minimum $E_{\text{TRANS}} = 0.3$ eV, required for it to surmount the 0.3 eV barrier to motion along the Cu-row.

Figure 14. Number of successful and abortive CF$_2$ + CF$_2$ association reactions at $b = 0$ Å as a function of CF$_2$ projectile recoil-distance before encountering a CF$_2$ target. If the CF$_2$ target was located less than ~10 Å from CF$_3$, only association reaction was observed. For CF$_2$ targets located more than ~10 Å from CF$_3$, a mixture of successful and abortive outcomes were observed.

The CF$_2$ + CF$_2$ collision with $b = 0$ Å was studied as a function of projectile collision energy ($E_{\text{col}}$) by varying the recoil distance of the projectile ($d_{\text{rec}}$) prior to its collision with the target. As shown in Figure 14 above, two collision-energy regimes were identified. Collision in the high $E_{\text{col}}$ regime due to $d_{\text{rec}} < \sim 10$ Å gave 100% probability of observing the association reaction. In contrast, collision in the low $E_{\text{col}}$ regime corresponding to $d_{\text{rec}} > \sim 10$ Å gave both association reaction and abortive reaction. The abortive reaction encounter at $b = 0$ Å, shown in Figure 15 below, caused the target to recoil along the direction of the projectile by $<d> = 13.1 \pm 4.6$ Å. The dynamics of the association reaction in the high $E_{\text{col}}$ regime was found to be different from the dynamics in the low $E_{\text{col}}$ regime as shown in Figure 16 below. Collision in the high $E_{\text{col}}$ regime ($d_{\text{rec}} < \sim 10$ Å) gave C$_2$F$_4$ that mainly recoiled ‘forward’, along the projectile direction, whereas low $E_{\text{col}}$ ($d_{\text{rec}} > \sim 10$ Å)
gave ‘backward’ recoiled C₂F₄. We shall show below by MD calculations that these two dynamics can be accounted by two collision energy regimes.

**Figure 15.** STM images (EXPT) of the CF₂ + CF₂ abortive reaction due to collision at low E_{col} regime. Panels (a) and (b) show the initial and final states of the abortive reaction. The white cross in (a) and (b) indicates the position where the tip was placed to generate the CF₂ projectile from the CF₃. The white solid arrow in (a) and dashed arrow in (b) indicate the recoil distance and direction of the CF₂ projectile. The black arrow in (b) indicates the recoil distance and direction of the CF₂ target from its initial position (black cross) along from the projectile approach direction. The STM images (2.1 × 4.7 nm²) were obtained at sample bias of −0.05 V and current of 0.05 nA.
Figure 16. Two pathways of CF$_2$ + CF$_2$ association reaction based on the observed C$_2$F$_4$ recoil direction. Panel (a) illustrates the coordinate system. The direction of motion of the CF$_2$ projectile before it collides with the CF$_2$ target (blue line in Panel (a), denoted as $d_{rec}(\text{CF}_2;\text{proj})$) was found to correlate with the recoil direction of the C$_2$F$_4$ product. The recoil of C$_2$F$_4$ ($d_{rec}(\text{C}_2\text{F}_4)$) measured from the prior position of CF$_2$ target (horizontal dashed line in Panel (a)), can be either ‘forward’ or ‘backward’. Panel (b) shows the C$_2$F$_4$ recoil ($d_{rec}(\text{C}_2\text{F}_4)$, red axis) plotted against the recoil distance of the CF$_2$ projectile ($d_{rec}(\text{CF}_2;\text{proj})$, blue axis); low $d_{rec}$ corresponds to high $E_{col}$, high $d_{rec}$ to low $E_{col}$.

5.2.4 Surface-aligned reaction of CF$_2$ + CF$_2$: Theory

MD calculations were employed to interpret the characteristic outcomes observed in the two $E_{col}$ regimes, which correspond to two ($E_{\text{TRANS}} + E_{\text{ROT}}$) regimes of the projectile. The three different outcomes observed in the experiment; ‘forward’, ‘backward’ and abortive reactions were reproduced in the trajectory. The calculations show that the ‘forward’ association reaction observed in the high $E_{col}$ regime is caused by successful C-C bond formation at the first CF$_2$ + CF$_2$ encounter with retention of the forward momentum of the CF$_2$ projectile. At close approach the
CF₂ projectile rotates, as in ‘ratchet’ dynamics, with $E_{\text{ROT}} \sim 0.6$ eV to overcome the energy barrier to form a C-C bond. By contrast, in the low $E_{\text{col}}$ regime, both the ‘backward’ reaction to form recoiling C₂F₄ and the abortive reaction scattering the CF₂ projectile backward involve failure to react at the first projectile + target encounter. In the case of ‘backward’ scattered C₂F₄ product the C-C bond is found to be formed at the second CF₂ + CF₂ encounter, with the reaction catalyzed by a raised Cu-atom. In abortive reaction the target CF₂ received translation energy from the first CF₂ + CF₂ encounter that was sufficient for it to surmount the diffusion barrier of 0.3 eV along the Cu-row.

The trajectories were obtained by varying the recoil distance of the projectile prior to its collision with the target. The initial state of the trajectory was set up by introducing a stationary ‘target’ CF₂ in its relaxed geometry into the path of the recoiling CF₂ projectile shown in Figure 6. The ‘forward’ reaction pathway, obtained in the high $E_{\text{col}}$ regime, was obtained by placing the CF₂ target ~3.5 unit cell (~8.8 Å) from the CF₃ precursor. The ‘backward’ reaction pathway, obtained in the low $E_{\text{col}}$ regime, was obtained when the CF₂ target was placed ~4.5 unit cell (~11.3 Å) from the CF₃ precursor. The abortive reaction pathway, observed in the low $E_{\text{col}}$ regime, was obtained when the CF₂ target was placed ~6.5 unit cell (~16.3 Å) from the CF₃ precursor. In all these three trajectories, the CF₂ projectile ‘ratchets’ towards the CF₂ target to its closest approach distance (~2.6 Å, ~1 unit cell), followed by the projectile frustrated rotation, swinging its C-atom towards the target CF₂ with varied $E_{\text{ROT}}$ that leads to the three different outcomes observed in the experiment. Below, we shall show the effect of varying $E_{\text{ROT}}$, which is crucial for C-C bond formation, and $E_{\text{TRANS}}$, which governs the center-of-mass motion of the product.
Figure 17. Computed dynamics for the ‘forward’ pathway in the CF$_2$ + CF$_2$ association reaction. The initial state (t = 0 fs) in this trajectory is constructed by introducing a zero-velocity CF$_2$ target into the I2S trajectory of a recoiling CF$_2$ projectile from Figure 6 at 163 fs. The CF$_2$ projectile reacts with CF$_2$ target on its first collision, giving a C$_2$F$_4$ recoiling ‘forward’. The grey vertical dashed line indicates the initial position of the center-of-mass of the CF$_2$ target.

The ‘forward’ reaction pathway obtained in the high E$_{col}$ regime is characterized by successful C-C bond-formation at the first CF$_2$ + CF$_2$ encounter as shown in Figure 17. In the trajectory, the projectile ratchets towards the target to bring the projectile to its closest approach distance to the target, as shown in the first 200 fs in Figure 17. At this closest approach distance, the projectile rotates, as a part of frustrated rotation in the ‘ratchet’ dynamics, swinging its C-atom from a Cu-atom to the C-atom of the target with an E$_{\text{ROT}}$ = 0.64 eV. This energy, as will be discussed in detail in the next paragraph, is sufficient to surmount the energy barrier to form a C-C bond. As a result of successful C-C bond formation, the residual E$_{\text{TRANS}}$ = 0.93 eV in the projectile is redistributed around the modes of the chemisorbed C$_2$F$_4$ product, of which 0.15 eV goes to the center-of-mass translation of C$_2$F$_4$ along the ‘forward’ direction.

The C-C bond formation, in the ‘forward’ trajectory, began from the configuration where both CF$_2$ were located on adjacent short-bridge sites of the same Cu-row. As shown from Panel 1 to 3 in Figure 18 below, the C-C bond formation began by having the CF$_2$ projectile rotated, as a part
of its frustrated rotation in the ‘ratchet’ dynamics, to direct its C-dangling bond towards the C-atom of the target, which then caused the CF$_2$ target to rotate towards the projectile, forming the C-C bond. These dynamics can be visualized in the landscape of a potential-energy surface (pes) plotted in the CF$_2$ rotational-coordinate space given in Figure 18. This pes was constructed by computing the potential energy as a function of rotational angles of the CF$_2$ projectile and the CF$_2$ target at their closest approach distance of 1 unit cell. In the ‘forward’ trajectory, the C-C bond successfully formed because the E$_{\text{ROT}}$ of the CF$_2$ projectile of 0.64 eV at its closest approach distance to the CF$_2$ target (see Panel 1) was sufficient to surmount the ~0.5 eV reaction barrier, as detailed below.

Figure 18. Computed trajectory for ‘forward’ reaction superimposed on a restricted ground PES. The 2D-PES is constructed as a function of CF$_2$ projectile and CF$_2$ target tilt angles at constant center-of-mass separation. The computed trajectory, given as red line, involves the motion of 78 atoms in the system. The insets give the nuclear positions in the angle-angle space for the computed trajectory at different times, showing both CF$_2$ at their closest approach distance at 240 fs in Panel 1, the transition state at 265 fs in Panel 2, and the C$_2$F$_4$ product at 290 fs in Panel 3. The dotted black lines in all Panels indicate C-Cu bond direction to an underlying Cu-atom. The dotted red line in Panel 2 indicates attraction at the inception of C-C bond formation, as evidenced by the negative slope of the potential towards the C$_2$F$_4$ product potential well at the transition state.

By superimposing the computed trajectory onto the 2D pes as shown in Figure 18, the CF$_2$ + CF$_2$ collision dynamics can be described by the CF$_2$ projectile rotation, barrier climbing (Panel 1 to 2), followed by the CF$_2$ target rotation with energy release due to C-C bond formation (Panel 2 to 3). The barrier climbing step is characterized by the stretching of a C-Cu bond as the projectile rotates to bring its C-atom further from the underlying Cu-atom, and closer to the C-atom of the target. At the transition state (Panel 2, Figure 18), the CF$_2$ projectile exerts C-C attraction towards
the CF₂ target. The C-C attraction caused the CF₂ target to rotate towards the projectile, leading to concurrent C-C bond formation and C-Cu bond breaking, as shown in Panel 2 to 3 of Figure 18.

Figure 19. Computed dynamics for a ‘backward’ product scattering pathway in the CF₂ + CF₂ association reaction. The initial state (t = 0 fs) in this trajectory was constructed by introducing a zero-velocity CF₂ target into the I2S trajectory of a recoiling CF₂ projectile from Figure 6 at 179 fs. The CF₂ projectile fails to react with the CF₂ target at the first collision. The second CF₂ + CF₂ collision, catalyzed by a raised Cu-atom, forms a ‘backward’ recoiling C₂F₄. The grey vertical dashed line indicates the initial position of the center-of-mass of the CF₂ target. The dashed circle behind the raised Cu-atom indicates the equilibrium position of the Cu-atom.

The ‘backward’ reaction pathway obtained in the low $E_{\text{col}}$ regime is characterized by successful C-C bond-formation at the second CF₂ + CF₂ encounter, catalyzed by a raised Cu-atom, as shown in Figure 19. At 400 fs, the trajectory shows a failed first CF₂ + CF₂ encounter due to the projectile possessing $E_{\text{ROT}} = 0.36$ eV, which is insufficient to surmount the ~0.5 eV association barrier. The abortive C-C bond formation caused the target to be repelled away from the projectile, and the Cu-atom between the projectile and the target to rise as high as ~1 Å. As shown from 600 fs to 800 fs, due to attraction between the target CF₂ and the raised Cu-atom, the target motion, which was initially ‘forward’, was reversed to ‘backward’, towards the projectile giving the second CF₂ + CF₂ encounter. As shown from 1200 fs to 1400 fs, this second encounter in which the target CF₂
approached the internally excited CF$_2$ projectile, is catalyzed by a Cu-atom raised as high as ~0.6 Å, which results in a C-C bond formation. Following the successful C-C bond formation, the residual $E_{\text{TRANS}} = 0.26$ eV in the target CF$_2$ moving in the ‘backward’ direction, was redistributed among the C$_2$F$_4$ modes, of which ~0.1 eV went to the C$_2$F$_4$ translation in the ‘backward’ direction.

The abortive reaction pathway, obtained in the low $E_{\text{col}}$ regime is characterized by facile momentum transfer from the projectile to the target. The trajectory shows a failed first CF$_2$ + CF$_2$ encounter due to the projectile possessing $E_{\text{ROT}} = 0.24$ eV which is insufficient to surmount the ~0.5 eV barrier to association. This abortive C-C reaction is followed by facile momentum transfer from the CF$_2$ projectile to the CF$_2$ target, which transferred $E_{\text{TRANS}} = 0.45$ eV from the projectile to the target along the ‘forward’ direction. As a result, the target CF$_2$ possessed enough energy to surmount the 0.3 eV diffusion barrier, allowing the target CF$_2$ to diffuse away from the projectile along the Cu-row.

### 5.3 Conclusions

Surface-Aligned Reaction (SAR) between a mobile CF$_2$ projectile and a stationary CF$_2$ target was studied on Cu(110) at 4.6 K. Chemisorbed CF$_3$ was used as a precursor to produce a recoiling CF$_2$ projectile. The electron tunneling to the CF$_3$-Cu hybrid state induced the C-F bond pointing along the Cu-row to break, giving a CF$_2$ that recoiled long distances undirectionally along a single Cu-row. The long distance CF$_2$ recoil was computed to be due repeated cycles of translation-rotation coupling within a CF$_2$ adsorbate molecule. The mechanism of long-range directed motion along a Cu-row was revealed to be ‘ratcheting’ in step 1 of which the dangling bonds of C bound chemically to a Cu-atom of the row rotating the CF$_2$ toward the surface (first engagement of the head of the ratchet) and in step 2 moved the two heavy F-atoms (engagement of the tail of the ratchet) translating the CF$_2$ along the row to a position in which the C could repeat step 1 by chemical binding to an adjacent atom of the same Cu-row to be followed thereafter by a further step 2. This succession of frustrated rotations followed by frustrated translations moves the CF$_2$ unidirectionally from one Cu-atom of a row to the next with a small energy loss to the surface, sustaining the motion for long distances (~20 Å in the computed trajectory, up to 50 Å experimentally). The closed-packed rows of Cu-atoms along the [110] direction of this anisotropic surface ensured that ratcheting took place unidirectionally along a row with a deviation of only ±1 degree, resulting in the new observation of highly-collimated surface-molecular-beams.
The collision between a CF$_2$ projectile and a CF$_2$ target was studied as a function of impact parameter ($b$) and collision energy ($E_{\text{col}}$). Collision with $b = 0$ Å was shown experimentally to result in CF$_2$ association reaction to give a chemisorbed C$_2$F$_4$, while collision with $b = 3.6$ Å gave an abortive reaction in which the target was repelled by the projectile, migrating to a new chemisorption site displaced in the forward direction. The zero impact-parameter ($b = 0$ Å) collision was studied as a function of collision energy $E_{\text{col}}$, by variation of the recoil-distance of the CF$_2$ projectile along a Cu-row. Two categories of association dynamics were distinguished experimentally by examining the recoil direction of C$_2$F$_4$ at the surface; ‘forward’ recoil (along the CF$_2$ projectile direction) at higher $E_{\text{col}}$, and ‘backward’ at lower $E_{\text{col}}$. Molecular dynamics (MD) calculations associated ‘forward’ scattering with a successful first CF$_2$ + CF$_2$ collision and ‘backward’ scattering with a failed first CF$_2$ + CF$_2$ encounter, followed by the successful second collision catalyzed by a raised Cu-atom. For an incoming CF$_2$ projectile colliding with a stationary CF$_2$ target, MD revealed two requirement for the reaction: (i) $b = 0$ Å, and $E_{\text{TRANS}} \geq 0.3$ eV to bring both CF$_2$ to their closest approach distance at ~2.6 Å, and (ii) $E_{\text{ROT}} > ~0.5$ eV, to overcome the barrier to association along the rotational coordinate. The rotational motion of the CF$_2$ projectile was needed to stretch the C-Cu bond to the surface and concurrently initiate C-C bond-formation with the target CF$_2$. This Surface-Aligned Reaction (SAR) study, by aiming a surface-molecular-beam at a stationary target with varied impact parameter and collision energy, gives fresh insight into the dynamics of an association reaction taking place at a metal surface.
Chapter 6
Thesis Conclusions

This thesis examines the effects surface anisotropy on the reaction dynamics of two small adsorbed molecules, meta-diiodobenzene (mDIB) and trifluoromethyl (CF$_3$) on Cu(110). The surface anisotropy, here given by rows of Cu-atoms along the [1\bar{1}0] direction of the Cu(110) surface, was found to give product rotation, bond selectivity and ‘surface-molecular-beams’. The reaction was initiated one-molecule-at-a-time by a tunneling electron, using STM at 4.6 K. The resulting dynamics were inferred by imaging the reagent molecule before and after the reaction. The dynamics were supported by MD calculations using the ‘Impulsive Two-State’ (I2S) model, which employed an empirical anionic potential-energy surface and an \textit{ab-initio} ground potential-energy surface.

The interaction between the I-atom in an iodophenyl (IPh) with the anisotropic surface was shown to induce its in-plane rotation. This was shown for the electron-induced reaction of mDIB as the parent molecule. In the major reaction pathway (97%), the reaction broke a C-I bond to give an IPh product that rotated in-plane to three different extents. The rotation was confirmed by dissociating the C-I bond in the three differently-rotated IPh, which was found to deposit I-atoms at three different positions. Calculations showed that the rotation was caused by attraction between the I-atom of IPh to the surface Cu-rows. A minor reaction pathway was also observed (3%), which gave two C-I bond-breaking, propelling the two I-atoms along the prior bond of the un-rotated molecule which had promptly dissociated. Since the extent of in-plane rotation of an IPh is indicative of the duration of the rotation, we propose this as a means of ‘clocking’ dynamics. Reaction dynamics could be time-resolved by initiating the IPh rotation by electron-induced mDIB dissociation, and, after a known time-delays, terminating the IPh rotation by a second electron-induced IPh dissociation, i.e. by a two-pulse correlation scheme. Following this time-resolved stage the extent of IPh rotation could be obtained by measuring I-atoms recoil angles using a conventional STM. The proposed scheme is intended to enable the study of time-resolved reaction dynamics without need for a time-resolved STM.

Directed recoil of a product on the anisotropic surface was shown to give a high degree of bond-selectivity. This was shown in the electron-induced reaction of mDIB adsorbed with one C-
I bond directed along the Cu-row, and the other C-I bond directed across the row. The C-I bond along the Cu-row was found to be hundred-times more likely to react than the C-I bond across the row. This selectivity was attributed to the directed motion of the system on the ground potential-energy surface (pes) along the C-I stretching coordinate. A restricted pes mirroring the dynamics showed a lower C-I dissociation barrier along the Cu-row ($E_a = 0.7$ eV) as compared to that across the Cu-row ($E_a = 1.5$ eV). The lower barrier was attributed to the stabilization of the transition state due to bonding with a nearby Cu-atom while the C-I bond was broken. This pathway was noted to be characteristic of the impulsive electron-induced process, being inaccessible to thermally induced reaction. It follows that electron-induced reactions, such as those common in photocatalytic systems, can give selective reaction pathways inaccessible to thermally-induced reactions.

In a novel finding it was shown that directional bonding of an adsorbate to an anisotropic surface can lead to electron-induced unidirectional recoil of product fragments for long distances, enabling them to be utilized as ‘projectiles’ aimed towards immobile ‘target’ molecules in studies of Surface-Aligned Reactions (SAR). This was shown in the electron-induced reaction of a chemisorbed CF$_3$ which broke a C-F bond pointing along a Cu-row to give a CF$_2$ projectile that recoiled unidirectionally with an angular dispersion of only $\pm 1^\circ$ along that row. In traversing the surface for long distances the recoiling CF$_2$ projectile coupled its translation and rotation to give linear motion. The linear motion of this collimated surface-beam was analyzed as being due to a succession of ‘ratcheting’ motions in which each ratcheting event comprised rotational motion of the C-atom binding successively to a pair of adjacent Cu-atoms of a row (comprising the claw of the ratchet) followed by a further step of motion in the same direction due to translation of the pair of heavy F-atoms. This sequence of rotational impulse followed by translational motion were shown to be sustained in the MD simulation.

In further experiments, this CF$_2$ projectile was aimed at a stationary CF$_2$ target to study the CF$_2$ + CF$_2$ association reaction. The unique feature of this experiment was the ability to select the impact parameter ($b$) and the collision energy ($E_{col}$). The CF$_2$ + CF$_2$ collision at $b = 0$ Å, in which the collimated CF$_2$ projectile was aimed directly at the stationary CF$_2$ target, was found experimentally to form a C-C bond and hence a chemisorbed C$_2$F$_4$. In contrast, the CF$_2$ + CF$_2$ collision at $b = 3.6$ Å gave abortive reaction, in which the target molecule was repelled back along the approach direction of the projectile, due to its collision with the projectile. The CF$_2$ + CF$_2$
collision at $b = 0 \text{ Å}$ was studied experimentally as a function of $E_{\text{col}}$ by varying the recoil distance ($d_{\text{rec}}$) of the projectile, CF$_2$, prior to collision with the target. At short projectile recoil ($d_{\text{rec}} < \sim 10 \text{ Å}$) the CF$_2$ + CF$_2$ collision with high $E_{\text{col}}$ gave C$_2$F$_4$ that recoiled ‘forward’, further along the approach direction of the CF$_2$ projectile due to, as revealed by MD calculations, the product retaining some of the translational energy of the projectile. At low $E_{\text{col}}$, obtained from long projectile recoil of the CF$_2$ projectile ($d_{\text{rec}} > \sim 10 \text{ Å}$), the collision gave C$_2$F$_4$ observed to recoil ‘backward’, attributed by MD calculation to a secondary CF$_2$ + CF$_2$ collision in the presence of a raised Cu-atom observed in the trajectory, which appeared responsible for catalyzing the CF$_2$ + CF$_2$ association resulting in the chemisorbed product C$_2$F$_4$. In this low $E_{\text{col}}$ regime of the experiments, the collision occasionally failed to form C$_2$F$_4$, resulting instead in the diffusion of the CF$_2$ target further along the projectile approach direction. The trajectory gave evidence of facile translational energy transfer from projectile to target, carrying the target CF$_2$ away, a further step across the Cu-row (across a 0.3 eV diffusion barrier). In summary the MD calculation showed that the requirement for reactive collision between an incoming projectile and a stationary target involved: (i) $b = 0 \text{ Å}$ and $E_{\text{TRANS}} > 0.3$ eV, required to bring both CF$_2$ to their closest approach distance of $\sim 2.6 \text{ Å}$ (~1 unit cell apart); and (ii) $E_{\text{ROT}} > 0.5$ eV, required to rotate the CF$_2$ projectile to initiate the C-C bond formation with the target CF$_2$. These results highlight the capability of SAR studies, by varying the impact parameter and the collision energy, to uncover the bimolecular reaction dynamics operating at a surface.

The method described here can readily be generalized to investigate other projectile + target pairs. As shown in the following Appendix A, we have already performed preliminary experimental SAR studies of the following four projectile + target pairs: (1) CF$_2$ + I; (2) F + I; (3) F + CF$_2$; and, (4) F + CF$_3$. Inelastic collision was observed in cases (1) and (2), while reactive collisions were observed in SAR (3) and (4).
Appendix A
Additional Surface-Aligned Reactions

7.1 CF₂ projectile + I-atom target ($b = 1.8$ Å): an inelastic collision

The CF₂ projectile characterized in Chapter 5 was aimed towards a chemisorbed I-atom. As shown in Figure S1 below, the reaction of CF₃ precursor caused the I-atom to be displaced by $2.4 \pm 0.3$ Å (~1 unit cell), from its initial four-fold hollow site to the next four-fold hollow site along the Cu-row direction. The I-atom diffusion can be understood to be caused by CF₂ + I collision since the CF₃ reaction was found to propel the CF₂ projectile towards the I-atom target. As shown in Figure S2, this outcome was only observed when the CF₃ – I separation was minimal ($d_{CF3-I} = 4.7 \pm 0.6$ Å); At longer separation, the I-atom did not diffuse, and acted as an obstacle which stopped the CF₂ recoil along the Cu-row. These observation are consistent with the notion that, at longer CF₂ – I separation, the CF₂ projectile would have lost some energy to the surface, resulting in weaker CF₂ + I collision that is insufficient to give I-atom diffusion.

![CF₂ + I SURFACE ALIGNED RXN](image)
**Figure S1.** STM images (EXPT) of CF$_2$ + I-atom SAR with $b = 1.8$ Å. Panel (a) shows a CF$_3$ precursor chemisorbed at ~4.7 Å away from an I-atom. The CF$_3$ adsorbed on a Cu-row (white dashed line), while the I-atom adsorbed between two Cu-rows at a four-fold hollow site. The white cross defines the position where the tip was placed to induce the CF$_3$ reaction, while the black cross defines the initial position of the I-atom target. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the outcome where I-atom was displaced by ~2.4 Å along the Cu-row direction. The STM images (2.2 × 2.7 nm$^2$) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.

**Figure S2.** Data tally of successful and failed I-atom displacement due to CF$_2$ + I collision with $b = 1.8$ Å as a function of CF$_2$ projectile recoil distance prior to its collision with the I-atom target. Successful I-atom displacement was only observed when the CF$_2$ projectile recoiled less than ~5 Å prior to its collision, indicating that successful I-atom displacement requires an energetic CF$_2$ projectile. Note that 3.8 Å is the nearest possible CF$_3$–I separation along [1$ar{1}$0] direction. Only cases where CF$_2$ was found within 2 unit cell along [1$ar{1}$0] from the I-atom in the final state were shown.

Preliminary DFT calculations suggested that, at short CF$_3$ – I separation shown in the STM image in Figure S1a, there is only one possible CF$_3$ – I relative configuration as shown in the molecular model given in Figure S1a. This computed structure suggests that the breaking of the C-F bond along the Cu-row in the CF$_3$ precursor would propel the CF$_2$ projectile *towards* the I-atom target. This CF$_2$ + I collision with an impact parameter ($b$) of 1.8 Å transferred energy from the CF$_2$ projectile to the I-atom target, which enabled the I-atom to overcome the diffusion barrier, computed to be at least 0.09 eV. Given that the translation energy of CF$_2$ from an isolated CF$_3$ computed at such short recoil distance was ~1 eV (see Figure 9 in Chapter 5), this preliminary result hence indicated that the CF$_2$ + I collision with $b = 1.8$ Å has a small (~10%) energy transfer efficiency. Further experiments and calculations are required to ascertain these preliminary claims.
7.2 F-atom projectile + I-atom target ($b = 3.3$ Å): an inelastic collision

Aside from CF$_2$ + I collision (see Appendix A1), I-atom diffusion can also be caused by F + I collision. As shown in Figure S3, the reaction of CF$_3$ precursor caused the I-atom target to diffuse; Since this reaction was found to propel the CF$_2$ product away from the I-atom target ($<d_{CF_2}> = 12.9 \pm 7.2$ Å), the I-atom diffusion was attributed to the F + I collision. This outcome was only observed when the CF$_3$ – I separation was minimum ($<d_{CF_3,I}> = 4.6 \pm 0.5$ Å); This initial state, shown in Figure S3a, is noted to be indistinguishable from that shown in Figure S1a, implying that the geometry of the initial state in both cases can be identical, as indicated by the identical molecular model in Figure S1a and S3a.

Figure S3. STM images (EXPT) of F + I SAR with $b = 3.3$ Å. Panel (a) shows a CF$_3$ precursor chemisorbed at ~4.6 Å away from an I-atom. The CF$_3$ adsorbed on a Cu-row (white dashed line), while the I-atom adsorbed between two Cu-rows at a four-fold hollow site. The white cross defines the position where the tip was placed to induce the CF$_3$ reaction, while the black cross defines the initial position of the I-atom target. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the outcome where I-atom was displaced by ~2.6 Å along the Cu-row direction. The STM images (3.4 × 4.1 nm$^2$) were obtained at sample bias of –0.05 V and current setpoint of 0.05 nA.
The product distribution, given in Figure S4 below, shows that the I-atom diffused by 2.6 ± 0.4 Å (~1 unit cell) along the Cu-row direction, from the initial four-fold hollow site to the next four-fold hollow site. As shown in Figure S4, this diffusion event was found to correlate with the F-atom being found on the adjacent Cu-row ($d_{F} = 3.6 \pm 0.9$ Å; $\theta_{F} = +105^\circ \pm 15^\circ$ from [110]). By superimposing the computed C-F bond directions of the CF$_3$ precursor, the F-atom was found along the direction of C-F bond across the Cu-row ($\theta_{CF,ACROSS} = +111^\circ$). This suggests that the I-atom diffusion can be caused by the collision between the I-atom target with the F-atom projectile with $b = 3.3$ Å, generated from the breaking of C-F bond across the Cu-row. Further calculations are required to confirm this preliminary claim.

**Figure S4.** Polar plot showing the angle and distance of I-atom target and the products in F + I SAR. The white cross indicates the position of the CF$_3$ precursor, while the red squares indicate the position of the I-atom relative to the CF$_3$. The data has been folded such that the I-atom target appears between 90° and 180°. The reaction of CF$_3$ precursor broke a single C-F bond, giving an F-atom (green squares), and a CF$_2$ that recoiled along [110] (not shown). This reaction caused the I-atom to be displaced to a new position (blue squares). The computed C-F bond directions in the CF$_3$ precursor is given as dashed lines. The distance between the concentric circles is 3.61 Å.

In summary, the initial state with such short CF$_3$ – I separation, as shown in Figure S1a and S3a, was found to give at least two reaction pathways: (1) the C-F bond along the Cu-row broke to propel CF$_2$ towards the I-atom, giving CF$_2$ + I collision (shown in Section 7.1); or (2) the C-F bond across the Cu-row broke to propel CF$_2$ away from the I-atom, giving F + I collision. We also observed Pathway (3) where the CF$_2$ was propelled away from the I-atom, but the I-atom was not displaced, rendering unclear which C-F bond in the CF$_3$ precursor was broken. The probability to observe Pathway (1), (2) and (3) was 16%, 56%, and 28% respectively. By contrasting this with
the reaction of an isolated CF₃, which consistently dissociates its C-F bond along the Cu-row, this finding implies that the presence of an I-atom next to a CF₃ introduces a new, and more favorable, bond-selective reaction pathway which breaks C-F bond across the Cu-row direction. This finding may establish the role of halogen atom, often thought as an inhibitor which blocks active sites on surfaces, as a *catalyst* for a surface reaction, by way of opening a new bond-selective reaction pathway. Such phenomenon was previously hinted at the study of reactions between ethene and oxygen on a Ag-surface, in which the presence of Cl-atoms on the surface made the reaction more selective towards the epoxidation pathway, instead of the combustion pathway.¹⁴⁹

### 7.3 F-atom projectile + CF₂ target (b = 0 Å): a reactive collision, producing a CF₃

![Figure S5](image_url)

**Figure S5.** STM images (EXPT) of F + CF₂ SAR with b = 0 Å. Panel (a) shows a CF₃ precursor chemisorbed ~4.2 Å away from the CF₂ target. Both the CF₃ precursor and the CF₂ target were adsorbed on the same Cu-row (white dashed line). The white cross defines the position where the tip was placed to induce the CF₃ reaction. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the SAR outcome where a CF₃ product was formed on the same Cu-row. The STM images (2.8 × 3.4 nm²) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.
The F-atom projectile was aimed at a stationary CF₂, producing a CF₃ product via F + CF₂ association reaction. As shown in Figure S5, the reaction of the CF₃ precursor next to the CF₂ target produced a CF₃ product. As the reaction of CF₃ was found to produce a CF₂ that was propelled away from the CF₂ target, the newly produced CF₃ was understood to be the result of a collision between an F-atom projectile, and the CF₂ target. This outcome was only observed when the CF₃ – CF₂ was minimally separated (<d_{CF₃-CF₂} = 4.2 ± 0.3 Å, ~1.5 unit cell) along the same Cu-row. At such separation, preliminary DFT calculations give the relative orientation of the CF₃ precursor and the CF₂ target shown in the molecular model of Figure S5a. The result suggested that the C-F bond along the Cu-row direction in the CF₃ precursor was broken to give F + CF₂ collision with impact parameter (b) of 0 Å, which produced a new CF₃ via the formation of a new C-F bond. Further experiment and calculations are required to confirm these preliminary claims.

7.4 F-atom projectile + CF₃ target (b = 0 Å): a reactive ‘knock-on’ collision, producing a CF₃ and an F-atom

**Figure S6.** STM images (EXPT) of F + CF₃ SAR with b = 0 Å. Panel (a) shows a CF₃ precursor chemisorbed ~7.6 Å away from the CF₃ target. Both the CF₃ precursor and the CF₃ target were adsorbed on the same Cu-row (white dashed line). The white cross defines the position where the tip was placed to induce the reaction of the CF₃.
precursor, the black cross defines the initial position of the CF<sub>3</sub> target. Molecular models are given next to the STM image to illustrate the objects identified on the surface. Panel (b) shows the SAR outcome, which consists of an F-atom product and a CF<sub>3</sub> product. The CF<sub>3</sub> product was found between the prior positions of the CF<sub>3</sub> precursor and the CF<sub>3</sub> target on the same Cu-row. The STM images (4.3 × 5.1 nm<sup>2</sup>) were obtained at sample bias of −0.05 V and current setpoint of 0.05 nA.

The F-atom projectile was aimed at a stationary CF<sub>3</sub> to produce a ‘knock-on’ reaction: a formation of a new C-F bond, concurrent with the breaking of an old C-F bond, in the CF<sub>3</sub> target in an S<sub>N</sub>2-like mechanism (Walden inversion mechanism<sup>150</sup>). As shown in Figure S6, the reaction of the CF<sub>3</sub> precursor next to the CF<sub>3</sub> target produced a new CF<sub>3</sub> product at a different position, and an F-atom product next to it. Given that the reaction of the CF<sub>3</sub> precursor propelled a CF<sub>2</sub> away from the CF<sub>3</sub> target, the newly produced CF<sub>3</sub> and F-atom is thought to be due to a collision between an F-atom projectile, and the CF<sub>3</sub> target. This outcome was observed when the CF<sub>3</sub> – CF<sub>3</sub> separation was ~7.6 Å (~3 unit cells) along the same Cu-row. The result hinted that F + CF<sub>3</sub> collision with impact parameter (b) of 0 Å produced a new CF<sub>3</sub> and F-atom via concurrent formation of a new C-F bond and breaking of an old C-F bond. Further experiments are required to confirm these preliminary claims.
Appendix B
Bonding Descriptions for F, CF₂ and C₂F₄

Figure S1. Computed adsorption structures for F, CF₂, chemisorbed tetrafluoroethylene, C₂F₄, and physisorbed C₂F₄ shown as molecular models viewed from the top (PIC (TOP)) and the side (PIC(SIDE)). The C₂F₄ is ‘BENT’ is the chemisorbed state. Also shown from the side is the charge density difference (Δρ) namely the change in electron distribution upon molecular adsorption (Δρ = ρ_{adsorbate+surface} − ρ_{adsorbate} − ρ_{surface}). The color scale corresponds to charge gain of +0.02 e⁻ Å⁻³ (given as red), and charge loss of −0.02 e⁻ Å⁻³ (given as blue).

Using DFT, the F-atom was computed to adsorb on a shortbridge site (i.e. between two Cu-atoms along the Cu-row direction). The charge-density difference of the F adsorption shown in Figure S1a involves electron accumulation around the F nucleus, indicative of ionic bonding. This is corroborated by the Bader charge-analysis which revealed that the F-atom possessed −0.71 charge as defined by Bader, with an opposing charge of +0.29 on both the nearest Cu-atoms, consistent with the previous calculations by Migani and Illas who studied the bonding structure of halogens on low-index metal surfaces.¹⁵¹
Figure S2. Gas-phase frontier molecular orbital of CF₂ and ‘BENT’ C₂F₄ showing the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) (isocontour: 0.007 e⁻Å⁻³). The calculations were performed using Gaussian16.

Difluorocarbene (CF₂) was computed to adsorb on a shortbridge site. The charge density difference of CF₂ adsorption shown in Figure S1b shows electron accumulation between the C nucleus and Cu nuclei, indicative of a covalent bonding which can be understood as the interaction of its frontier molecular orbitals (HOMO and LUMO shown in Figure S2a above) to the Cu d-orbitals. Similar to the Blyholder model of CO adsorption on metal surfaces¹⁵², the interaction consists of electron donation from CF₂ HOMO, which resembles the sp²-like C-dangling bond orbital, to the Cu, mainly via the dₜₛ orbital; and back-donation from the Cu, mainly via the dₜ₂ orbital to the CF₂ LUMO, which resembles the empty p-orbital in the C-atom. The y-axis in the preceding discussion is the [1̅10] direction.

Similar analysis performed on the chemisorbed tetrafluoroethylene (C₂F₄) showed that the molecule was covalently bonded to a single Cu-atom as in Figure S1c. The bonding is best described by the interaction of its frontier molecular orbital (HOMO and LUMO shown in Figure S2b above) with the Cu d-orbitals. The HOMO and LUMO of the chemisorbed C₂F₄ are described as π and π* orbitals, with some s-character mixed into them due to the bending of the C-F bonds. The C₂F₄ bonding with the surface is consistent with the Dewar-Chatt-Duncanson model of ethylene bonding to a metal atom¹⁵³,¹⁵⁴, where the C₂F₄ HOMO donates charge to the Cu, mainly via its dₜ² orbital; and the C₂F₄ LUMO receives back-donation from the Cu, mainly via its dₜ₂ orbital. Here y-axis is again the [1̅10] direction.

In contrast to the chemisorbed C₂F₄, the physisorbed C₂F₄ did not possess covalent or ionic bonds to the surface. This is evidenced by the lack of electron rearrangement in the charge-density difference shown in Figure S1d. The molecule only interacts with the surface via van der Waals bonding.
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